**FACULTY OF ENGINEERING AND SUSTAINABLE DEVELOPMENT**

# STUDY OF FACTORS INFLUENCING THE QUALITY AND YIELD OF BIODIESEL PRODUCED BY TRANSESTERIFICATION OF VEGETABLE OILS

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# PREFACE

This paper is a final thesis for the Energy Systems Master Programme in the University of Gävle. It was carried out from March to June 2010 in the Faculty of Engineering and Sustainable Development which belongs to the university. This thesis could not have been completed without the help and support of many people, some of them are mentioned below.

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# ABSTRACT

Biofuels are a developing kind of fuel whose origin is biomass. Among them, many different kind of fuels can be found: bioethanol, biobutanol, biodiesel, vegetable oils, biomethanol, pyrolysis oils, biogas, and biohydrogen. This thesis work is focused on the production of biodiesel, which can be used in diesel engines as a substitute for mineral diesel. Biodiesel is obtained from different kinds of oils, both from vegetable and animal sources. However, vegetable oils are preferred because they tend to be liquid at room temperature.

The process to obtain biodiesel implies first a reaction between the oil and an alcohol, using a catalyst and then a sedimentation, where the biodiesel and the glycerol, the two products that are obtained, can be separated because of their difference in density. After the separation, raw biodiesel is obtained and a treatment with either water bubbling or dry cleaning products is needed to obtain the product which will be ready to use.

Many methods are available for the production of biodiesel, most of them require heat for the transesterification reaction, which converts the oil into biodiesel. Apart from that, in many cases biodiesel is produced by big companies or by individuals but using complicated and expensive installations.

This work is an attempt to develop a way of producing biodiesel without any use of external heat, using a simple procedure which could be used by people with a low knowledge of chemistry or chemical processes. It also seeks to set an example on how biodiesel can be easily made by oneself without the use of any industrial systems, with a low budget and limited need of supervision over the process.

In order to achieve that, many trials were undertaken, introducing changes in the different parameters that are responsible for the changes in the final product. Among them, changes in the amount and type of catalyst, the way the catalyst is added, the type of oil used, the time of reaction and the temperature were made. Apart from that, different types of cleaning were tried, starting by water cleaning and then using powder type products, Magnesol, D-Sol and Aerogel. A centrifuge was also tried to test its utility when separating impurities from liquids or different liquid phases. The results of the different trials were analysed using various tests, the most important being the 3:27 test, the solubility test, the soap titration and pH measurements.

To sum up, it could be said that the investigation was a success, since it was proved that biodiesel can be made without the use of any external heat with both alkali and acid catalysts, as well as with different ways of adding the catalyst. As for the cleaning, good results were obtained with both dry products and water cleaning, since the soap content of the biodiesel was reduced in both cases. Apart from that, the centrifuge proved to be valid to eliminate impurities from raw oil.

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# 1 INTRODUCTION

## 1.1 Background

Energy is one of the big worries of the humanity nowadays. In fact, not energy itself, but the sources of the energy. There are several issues around this topic. On the one hand, there is the always recurrent end of the oil era. For several years, warnings about the depletion of the oil reserves have been transmitted. However, nowadays, that is not a reality, or, at least, it is not a public reality. It is almost impossible to determine how long it will be possible to live in the petroleum era. Nevertheless, it is a reality that, eventually, the problem will have to be faced.

As if that was not enough, lately a new and very worrying matter has emerged: the global warming. It is believed that, due to the high dependancy on fossil fuels, the amount of carbon dioxide in the atmosphere is increasing. Thus, creating what is called the greenhouse effect, that prevents heat in the form of infrared radiation from leaving the earth. Because of this, the earth temperature is said to be increasing, this could cause several environmental catastrophes and maybe even change the earth as we know it now.

One of the options to reduce our effect on the global warming and, at the same time, minimise the oil dependency are biofuels. Biofuels have two advantages when compared to other energy sources: they are a renewable source of energy and they minimise the carbon dioxide emissions. Therefore, when using them, using oil and the troubles related to it are avoided. It must be said that biofuels are not the only solution. Actually, biofuels should never be regarded as if they were the solution to all problems. Biofuels are just one of the new energy sources that can change our energy consumption habits, but several other options are needed to achieve the objective of sustainability.

This paper focuses on biodiesel, which is a natural substitute to mineral diesel. Biodiesel is produced using different kinds of oil, including edible and non-edible vegetable oils, waste vegetable oils (residual oils used for cooking), animal fats and algae oils. Using a simple chemical procedure biodiesel can be produced. Afterwards, that biodiesel can be used blended with mineral diesel in different proportions or without blending, what is called B100, in diesel engines. Biodiesel is also suitable for direct burning.

There are several advantages when using biodiesel instead of mineral diesel, the most important ones are the following:

- It is an alternative to mineral diesel, implying lower dependence on foreign imports of crude oil.
- Biodiesel is a renewable fuel.

- It has a favourable energy balance. That is, more energy is obtained when using biodiesel in a diesel engine than the amount that is used for the production of the biodiesel.
- Using biodiesel helps reducing greenhouse gas emissions, as stipulated in the Kyoto Protocol agreement.
- Harmful emissions of biodiesel are lower than those of mineral diesel, especially important in environmentally sensitive areas like large cities.
- It is biodegradable and non-toxic. [1]

There is a final reason that prompted writing this paper. Most of the investigation work about biodiesel production has been carried out in a way that makes heat necessary for obtaining it. Therefore, no data could be found in the literature for the process taking place at room temperature. However, due to the importance of small-scale biodiesel producers, it would be very interesting if a process avoiding the use of heat was developed. In that way, both the equipment and the control of the process could be easily simplified, allowing everyone to produce their own biodiesel without too many complications. In response to this lack of information, this thesis is an attempt to prove that there is no need to use heat in order to produce biodiesel.

## 1.2 Purpose

The aim of this thesis is to explain what biodiesel is and to find the best conditions for producing biodiesel avoiding the use of heat. It includes the best reaction parameters as well as cleaning and purifying methods.

## 1.3 Limitations

The main limitation of this project is the difficulty to determine the quality of the produced biodiesel. To do so, gas chromatograph equipment is needed, unfortunately, there was no such equipment available, which has determined the final results. Therefore, it has not been possible to find out whether the produced biodiesel fulfils the specifications. However, some other simple tests have been used and the obtained results are positive.

It should also be mentioned that the economic aspect has not been given a foremost importance when conducting the investigation. Thus, even if the production of suitable/ desired quality biodiesel is guaranteed, it cannot be guaranteed it being economical.

## 1.4 Method

First of all, familiarisation with the biodiesel producing method had to be achieved. To do so, different trials were carried out, using different conditions and analysing the obtained results.

At the same time, to understand the process altogether, literature research was performed. This, apart from a better knowledge of what biodiesel is and its production implies, was a good source of how to avoid mistakes and simplify the laboratory process.

The next step was the proper laboratory research, which could be divided into three parts:

1. The first of them is the production of biodiesel. During this period, different trials on how to produce biodiesel were performed, changing reaction conditions, amounts of reagents and catalysts, etc.

2. The second period consisted on different trials with different cleaning methods for biodiesel. Both dry cleaning and water cleaning were tried. In the dry cleaning four different products were tested: Magnesol and D-Sol, both manufactured by the Dallas Group of America and two types of Aerogel, manufactured by Svenska Aerogel.

3. The third stage was devoted to determine the advantages of using a centrifuge in the process, mainly to see its performance in the separation of two-phase liquid mixtures or liquids with different kinds of impurities.

During the whole laboratory research different tests were made to understand the results obtained and improve the method.

Finally, when the all the tests were performed, the results were analysed and the best method to produce biodiesel without using heat was determined. This will allow implementing the process at a bigger scale.

## 1.5 Outline

The first section of the thesis, which is called ‘Vegetable oils as fuels’, is an introductory section in which it is explained the properties of vegetable oils and their constituents, as well as their sources. Apart from that, a justification for them not being used directly as fuels is given when talking about their disadvantages. Finally, different methods to improve the properties of vegetable oils for using them as fuels are explained, including transesterification.

Next comes a comprehensive chapter about biodiesel. In it, apart from defining what biodiesel is, the transesterification reaction is explained thoroughly, including reagents, catalysts, mechanism and conditions. Besides, there is an explanation on how to clean biodiesel including both dry and water cleaning and all the characteristics of biodiesel are stated. Eventually, the advantages and disadvantages of biodiesel are displayed.

The third chapter is the experimental procedure. As its name says, what was done in the lab is explained step by step, following the order of the biodiesel making process. It starts

with the titration. Then, comes the production of biodiesel, where all the different methods that were tried are explained. Afterwards is stated how the separation of the products and how the cleaning was done. This is followed by the explanation of the different tests that were done to verify the quality of the biodiesel. At last, the different trials that were done with the centrifuge are described.

Following the experimental procedure, there is a chapter that shows all the results obtained in the lab. The results of all the relevant experiments performed are presented, for the titration, production of biodiesel, cleaning, soap titration and use of the centrifuge.

After that, a discussion of the results is done, stating their validity and key factors that help to understand them. It is also discussed which are the best ways to produce biodiesel and the advantages and disadvantages of different methods. A section about methanol, an important issue when producing biodiesel, is also included.

The last chapter are the conclusions. In it, the interpretation of everything that was done to obtain this thesis is conducted, focusing on the key factors.

# 2 VEGETABLE OILS AS FUELS

The use of fuels whose source are vegetables is not a new discovery, more than one hundred years ago, Dr. Rudolf Diesel used peanut oil as fuel for his engine. In fact, Dr. Diesel designed the original diesel engine to run on vegetable oil [2, 3]. Vegetable oils were used in diesel engines until the 1920s. However, during that decade, the manufacturers of diesel engines changed their specifications so as to make them more suitable for the viscosity of mineral diesel instead of the previously used vegetable oils. There are several advantages in the use of vegetable oils as diesel, which are: portability; ready availability; renewability; higher heat content, lower sulphur content and lower aromatic content than that of mineral diesel; and biodegradability [3].

## 2.1 Constituents and properties of vegetable oils

The oils and fats are mixtures of liquids. Their main components of raw oils are usually triacylglycerols (generally > 95%) as well as diacylglycerols, monoacylglycerols and free fatty acids (FFA). Some other substances like phospholipids, free sterols and sterol esters, tocols, triterpene alcohols, hydrocarbons and fat-soluble vitamins may also be present [4]. The main difference between vegetable oils and animal fats is the fact that animal fats are usually saturated, that is, they do not have double-bonds, which makes them solid at room temperature. On the other hand, vegetable oils are usually liquid at room temperature.

The structure of vegetable oils differs from the structure of mineral diesel. In the case of the vegetable oils, as many as three fatty acids can be linked to a glycerol molecule using esters as linkers. Such molecules are the main constituent mentioned above, the triacylglycerols, while the diacylglycerols and monoacylglycerols refer to the cases when only two or one fatty acids are linked to a glycerol molecule. The fatty acids present in the oils will be different from each other, depending on their length and, also, on the number, orientation and position of the double-bonds [5, 6].

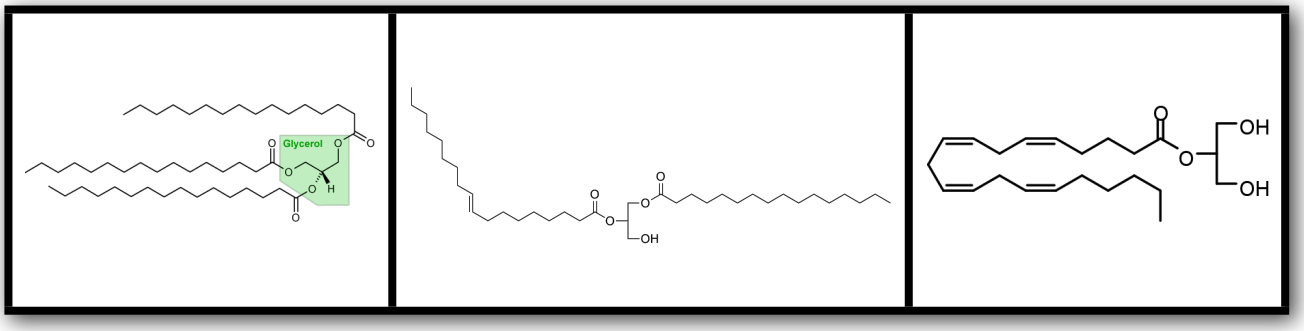


*Figure 2.1: A triacylglycerol, a diacylglycerol and a monoacylglycerol (from left to right) [7, 8, 9]*

## 2.2 Sources of oils and fats

There are several types of oils and fats and they can be classified depending on their source:

| Vegetable oils | Non edible oils | Animal fats | Other sources |
|---|---|---|---|
| Soybeans | Almond | Lard | Bacteria |
| Rapeseed | *Abutilon muticum* | Tallow | Algae |
| Canola | Andiroba | Poultry Fat | Fungi |
| Safflower | Babassu | Fish oil | Micro algae |
| Barley | *Brassica carinata* | | Tarpenes |
| Coconut | *B. napus* | | Laxetes |
| Copra | Camelina | | Cooking oil (yellow grease) |
| Cotton seed | Cumaru | | Microalgae (Chroellavulgaris) |
| Groundnut | *Cynara cadunculus* | | |
| Oat | Jatrophacurcas | | |
| Rice | *Jathropa nana* | | |
| Sorghum | Jojoba oil | | |
| Wheat | Pongamiaglabra | | |
| Winter rapeseed oil | Laurel | | |
| | Lesquerellafendleri | | |
| | Mahua | | |
| | Piqui | | |
| | Palm | | |
| | Karang | | |
| | Tobacco seed | | |
| | Rubber plant | | |
| | Rice bran | | |
| | Sesame | | |
| | Salmon oil | | |

*Table 2.1: Classification of oils depending on their source [10]*

More information on different kinds of oils and their properties can be found in the Annex I.

## 2.3 Disadvantages of vegetable oils when used as fuels

However, several difficulties have been found, mainly concerning the high viscosity of this kind of oil compared to the viscosity of mineral diesel [4], which usually leads to poor fuel atomisation, incomplete combustion, carbon deposition on the injector and fuel build up in the lubricant oils. Moreover, some other physical properties such as their lower volatility compared to mineral diesel and the reactivity of unsaturated hydrocarbon chains have led to the necessity of finding more suitable fuels [3, 11].

In table 2.2 a compilation of known problems when using vegetable oils as fuels as well as their probable cause and potential solution is shown:

| Problem | Probable cause | Potential solution |
|---|---|---|
| Short term | | |
| 1. Cold weather starting | High viscosity, low cetane and low flash point of vegetable oils | Preheat fuel prior to injection. Chemically alter fuel to an ester. |
| 2. Plugging and gumming of filters, lines and injectors | Natural gums (phosphatides) in vegetable oil. Other ash | Partially refine the oil to remove gums. Filter to 4-microns |
| 3. Engine knocking | Very low cetane of some oils. Improper injection timing | Adjust injection timing. Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester |
| Long term | | |
| 4. Coking of injectors on piston and head of engine | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. |
| 5. Carbon deposits on piston and head of engine | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils |
| 6. Excessive engine gear | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Increase motor oil changes. Motor oil additives to inhibit oxidation |
| 7. Failure of engine lubricating oil due to polymerisation | Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerisation starts | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Increase motor oil changes. Motor oil additives to inhibit oxidation |

*Table 2.2: Known problems, probable cause and potential solutions for using straight vegetable oil in diesels [12]*

## 2.4 Methods to improve the quality of vegetable oils

Due to the many problems derived from using vegetable oils as fuels, different methods have been developed to reduce their disadvantages, the most important being the following:

a. Dilution with a suitable solvent: it is done by diluting the vegetable oil with mineral diesel to run the engine.

b. Emulsification: also called microemulsion, it can be defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally into 1–150 range formed spontaneously from two normally immiscible liquids and one and more ionic or more ionic amphiphiles. They can improve spray characteristics by explosive vaporisation of the low boiling constituents in micelles.

c. Pyrolysis: with this method a substance can be converted into another using heat with the aid of a catalyst in the absence of oxygen or air. With that, a thermal decomposition of the oil takes place and the heaviest components of the oil are converted into lighter molecules, which reduces the viscosity. This method is also used to reduce viscosities of fuel oils and is known as visbreaking. [10]

d. Transesterification: it is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol [3]. After the reaction, two products are obtained, the main product is what is called biodiesel and the other is glycerol.

Of all the processes mentioned above, the transesterification is the one that gives better results when the purpose is to reduce the viscosity of oils. Furthermore, glycerol, which also has a commercial value, is obtained as a by-product. [13]

# 3 BIODIESEL

## 3.1 Definition

The term Biodiesel was first used in 1992 in the National Soy diesel Development Board (now called National Bio Diesel Board) in the United States [10]. Biodiesel is the name used to refer to a diesel-equivalent fuel that has been obtained from biological sources [4], using the transesterification reaction. Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids and is typically made from nontoxic, biological resources such as vegetable oils, animal fats, or even waste vegetable oils (WVO) [14].

## 3.2 Transesterification process

For the production of biodiesel, a vegetable oil or animal fat reacts with ethanol or methanol in the presence of a catalyst. From this, methyl or ethyl esters are obtained, which are the components of biodiesel. Along with the esters, glycerol is also produced [3]. That reaction is called transesterification. Stoichiometrically, when the reaction takes place, for every mole of triglycerides reacting, three moles of alcohol are used. However, a higher molar ratio of alcohol is usually used for maximum ester production [13]. This will be more precisely explained in the next pages of the report.

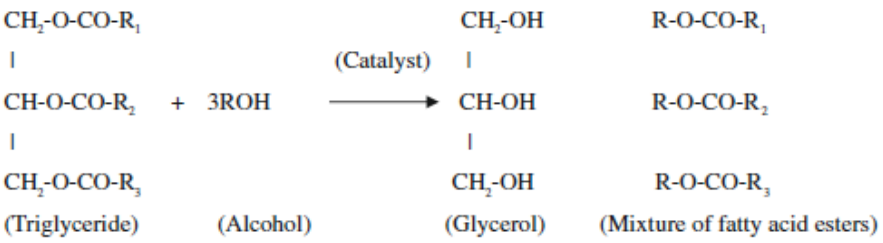


*Figure 3.1: Chemical equation of the transesterification mechanism [14]*

R1, R2 and R3 are long chain hydrocarbons, sometimes they are also known as fatty acids. In the presence of the catalyst, the alcohol molecule will be able to break the fatty acid chains, resulting in two different products, glycerol and a mixture of fatty acid esters [14].

### 3.2.1 Reagents

As shown in the reaction above, two reagents are needed, oil and an alcohol. The decision of which oil and which alcohol to use will depend on many different factors. In both cases, the availability of some kind of oil and/or alcohol, will probably define which one to use. However, in many cases, when the reagents to use have to be chosen, many different aspects have to be taken into account.

In the case of the alcohol, probably the most important reason is the money. Ethanol and methanol are the most commonly used alcohols, but methanol is usually preferred because it is cheaper [15]. Moreover, ethanol has a lower transesterification reactivity than methanol [14]. Of course, other alcohols could be considered, but their higher prices make them unsuitable, except for the cases when there is a cheap source available.

Choosing the oil is probably a more complex issue than choosing the alcohol. In this case many different factors have to be taken into account, not only the price. When commenting on the price it should be noted that the lower the price, the lower the quality of the oil. Usually, lower price means a high content of FFAs, which, as will be shown in the next chapters, involves a bigger production of soap, a by-product that is not interesting [16]. Furthermore, the soap may lead to difficulties in the reaction and separation of the products. The oils with higher amount of FFAs are usually waste vegetable oils, that is, oils that have been used for cooking purposes. In the case of clean vegetable oils, there should not be so high values of FFAs.

Other important motive to choose one type of oil over other is that the kind of biodiesel obtained depends highly on the oil that has been used to produce it. Table 3.1 shows the kinematic viscosity of different oils and biodiesel, obtained from different sources. It can be appreciated that the oil from which is obtained will affect in different ways the kinematic viscosity of the product.

| Species | Kinematic viscosity of oil (centistokes, at 40ºC) | Kinematic viscosity of biodiesel (centistokes, at 40ºC) |
|---|---|---|
| Rapeseed | 35.1 | 4,3-5,83 |
| Soybean | 32.9 | 4.08 |
| Sunflower | 32.6 | 4.9 |
| Palm | 39.6 | 4.42 |
| Peanut | 22.72 | 4.42 |
| Corn | 34.9 | 3.39 |
| Canola | 38.2 | 3.53 |
| Cotton | 18.2 | 4.07 |
| Pumpkin | 35.6 | 4.41 |

*Table 3.1: Comparison between the kinematic viscosoties of vegetable oils and the biodiesel obtained from the oils [14]*

As in the case of the kinematic viscosity, many other properties will vary depending on the source of vegetable oil. For additional information, examine Annex I.

Apart from that, there are some other important factors that must be taken into account. For instance, the possibility of obtaining a kind of vegetable oil depending on the geographical location and, indeed, the suitability of the biodiesel obtained from that oil depending on the climate conditions. As an example, palm oil is a good source for biodiesel when used in tropical countries, but, if it has to be used in Sweden, several problems could appear because of its high cloud point.

In some cases, when the producer of the biodiesel is also the producer of the oil, the choice might be which seed to grow instead of choosing the oil type. This is a very complex matter that will not be deeply analysed in this report, but there are two parameters which are easy to understand and may be helpful. The first of them is the production of seed per square meter that has been sown. The second is the yield of oil and meal obtained by extraction of the seed. In table 3.2 data for the second parameter of the major oilseeds can be seen:

| Oilseed | Oil | Meal |
|---|---|---|
| Soybean | 18.3 | 79.5 |
| Cottonseed | 15.1 | 57.4 |
| Groundnut | 40.3 | 57.2 |
| Sunflower | 40.9 | 46.9 |
| Rapeseed | 38.6 | 60.3 |
| Palmkernel | 44.6 | 54.0 |
| Copra | 62.4 | 35.4 |
| Linseed | 33.3 | 64.2 |

*Table 3.2: Yields (%) of oil and of meal obtained by extraction of the major oilseeds [4]*

As shown in the table, the variation on the yield of oil depending on the oilseed is significative. Thus, it should be considered when deciding the oilseed to use. In addition, other factors such as environmental conditions or geographical location should be contemplated.

In conclusion, choosing the oil is a complex process, which will be highly determined by its price, but some other factors should also be studied. Nevertheless, the amount of free fatty acids in the oil is a good point to start with, because it may cause several difficulties when making biodiesel. Therefore, using oil with low FFA content is always recommended. Since the cost of raw materials accounts for about 60–80% of the total cost of biodiesel production, choosing a right feedstock is very important [10].

### 3.2.2 Catalyst

The presence of a catalyst is mandatory for this chemical reaction to happen in normal conditions. Several types of catalysts have been tried, both heterogeneous and homogeneous. The homogeneous catalysts can be divided into two categories, alkalis and acids. The most common alkali catalysts are potassium hydroxide, potassium methoxide, sodium hydroxide and sodium methoxide. Alternately, the acid catalysts include products like sulphuric acid, hydrochloric acid and sulphonic acid.

The other group is formed by heterogeneous catalysts. It includes enzymes, titanium-silicates, alkaline-earth metal compounds, anion exchange resins and guanadines heterogeneisated on organic polymers [1].

A third option is also available, it is using supercritical methanol. In this case, no catalyst is needed, but, on the other hand, high temperature and high pressure conditions i.e. 573 K and 20 MPa, are needed [13].

Another option that should be mentioned is the use of ultrasonic reactors and microwaves. Ultrasonic reactors have been tried with good results, however, using a catalyst is still necessary [17]. As for microwaves, they are used combined with both heterogeneous and homogeneous catalysts, obtaining lower reaction times than when no microwaves are used [18, 19].

Depending on the type of catalyst used, several advantages and disadvantages will be found. The most widely used catalyst type are the alkalis and, among the alkalis, the most used is the potassium hydroxide. This is because with this kind of catalyst the process is fast and the conditions are moderate. However, the disadvantage appears is the formation of soaps, which are produced by neutralising the free fatty acid in the oil and triglyceride saponification. Both soap formations are undesirable side-reactions, because they partially consume the catalyst, decrease the biodiesel yield and complicate the separation and purification steps [1].

Acid catalysts have not been used as widely as alkali catalysts. Its main advantage is that the presence of free fatty acids will not affect the reaction. Moreover, acid catalysts can catalyse both esterification and transesterification at the same time. The esterification is a chemical reaction in which an alcohol and an acid react, producing an ester. This means that the FFAs, instead of producing soap as in the alkali catalysed reaction, will produce esters, which is the product of interest. However, there are some disadvantages that have induced the higher use of alkali catalysts, the most important are: a slower reaction rate, requirement of high reaction temperature, high molar ratio of alcohol to oil, separation of the catalyst, serious environmental and corrosion related problems [20].

The main advantage of the heterogeneous catalysts is that the post-treatment of the products is easier, because it facilitates the separation and minimises the purification. In addition, there is no production of soaps. On the contrary, it requires extreme reaction conditions and the low methyl ester yield and high reaction time are more favourable in the case of the alkali catalysed transesterification [1].

Table 3.3 is a summary of the different kinds of catalysts that can be used, as well as their advantages and disadvantages:

| Type of catalyst | Advantages | Disadvantages |
|---|---|---|
| Homogeneous base catalyst | Very fast reaction rate - 4000 times faster than acid-catalysed transesterification<br>Reaction can occur at mild reaction condition and less energy intensive<br>Catalysts such as NaOH and KOH are relatively cheap and widely available | Sensitive to FFA content in the oil<br>Soap will form if the FFA content in the oil is more than 2 wt%<br>Too much soap formation will decrease the biodiesel yield and cause problems during product purification especially generating huge amounts of wastewater |
| Heterogeneous base catalyst | Relatively faster reaction rate than acid-catalysed transesterification<br>Reaction can occur at mild reaction condition and less energy intensive<br>Easy separation of catalyst from product<br>High possibility to reuse and regenerate the catalyst | Poisoning of the catalyst when exposed to ambient air<br>Sensitive to FFA content in the oil due to its basicity property<br>Soap will be formed of the FFA content in the oil is more than 2 wt %<br>Too much soap formation will decrease the biodiesel yield and cause problems during product purification<br>Leaching of catalyst active sites may result in product contamination |
| Homogeneous acid catalyst | Insensitive to FFA and water content in the oil<br>Preferred method if low-grade oil is used<br>Esterification and transesterification occur simultaneously<br>Reaction can occur at mild reaction condition and less energy intensive | Very slow reaction rate<br>Corrosive catalyst such as $H_2SO_4$ used can lead to corrosion on reactor and pipelines<br>Separation of catalyst from product is problematic |
| Heterogeneous acid catalyst | Insensitive to FFA and water content in the oil<br>Preferred method if low-grade oil is used<br>Esterification and transesterification occur simultaneously<br>Easy separation of catalyst from product | Complicated catalyst synthesis procedures lead to higher cost<br>Normally, high reaction temperature, high alcohol to oil molar ratio and long reaction time are required<br>Energy intensive<br>Leaching of catalyst active sites may result to product contamination |
| Enzyme | Preferred method if low-grade oil is used<br>Transesterification can be carried out at low reaction temperature, even lower than homogeneous base catalyst<br>Only simple purification step is required | Very slow reaction rate, even slower than acid-catalysed transesterification<br>High cost<br>Sensitive to alcohol, typically methanol can deactivate the enzyme |

*Table 3.3: Advantages and disadvantages of different types of catalysts [20]*

### 3.2.3 Mechanism

The mechanism for the transesterification is a series of consecutive reversible reactions, where a triglyceride is converted stepwise to diglyceride, monoglyceride and, finally, glycerol. In each one of the steps a mole of ester is liberated. They are reversible

reactions even though the equilibrium tends toward the products, that is, glycerol and the free fatty esters.

Depending on the type of catalyst chosen, the mechanism of the reaction will vary. In the case of the alkali catalysed reaction, the mechanism was formulated in three steps, in the first of them the anion of the alcohol will attack the carbonyl carbon atom of the triglyceride and a tetrahedral intermediate will be formed. The second step implies that intermediate reacting with an alcohol to regenerate the anion of the alcohol. Finally, in the third step, a rearrangement of the tetraheldral intermediate takes place, resulting in the formation of a fatty acid ester and a diglyceride.

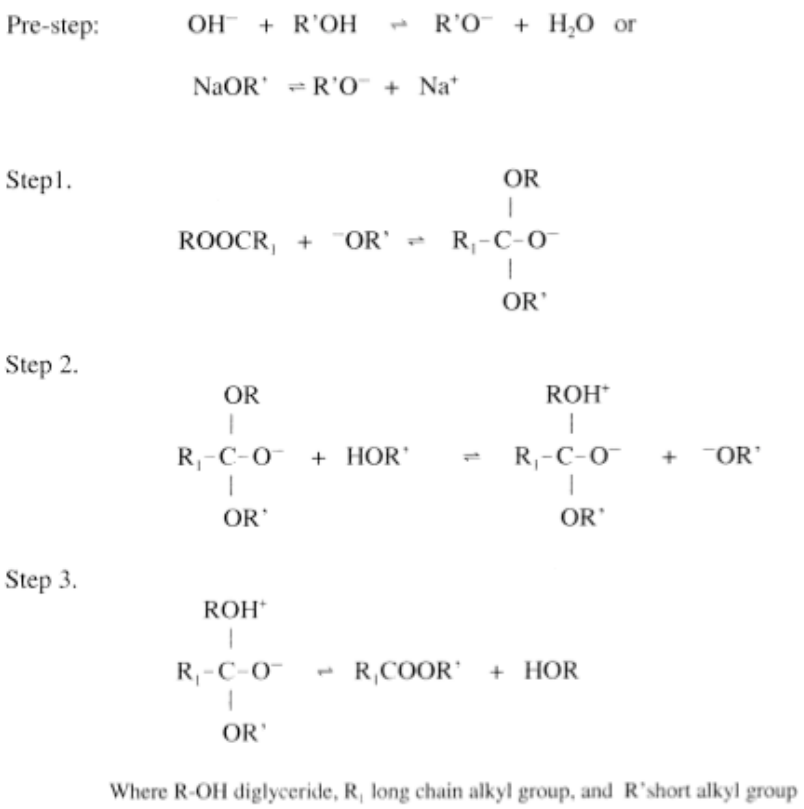
Pre-step:
OH⁻ + R'OH ⇌ R'O⁻ + H2O or
NaOR' ⇌ R'O⁻ + Na⁺
Step1.
ROOCR1 + ⁻OR' ⇌ R1-C(OR)(OR')-O⁻
Step 2.
R1-C(OR)(OR')-O⁻ + HOR' ⇌ R1-C(ROH⁺)(OR')-O⁻ + ⁻OR'
Step 3.
R1-C(ROH⁺)(OR')-O⁻ ⇌ R1COOR' + HOR
Where R-OH diglyceride, R1 long chain alkyl group, and R'short alkyl group

*Figure 1.3: The mechanism of the alkali catalysed transesterification [21]*

The catalyst is not the alkali itself, but the product created by mixing the alkali with the alcohol, which is an alkoxide group. When this reaction takes place a small amount of water is generated, which may cause problems due to soap formation during transesterification [21].

On the other hand, if the catalyst used is an acid, the mechanism will be defined by it, therefore, it will be an acid mechanism and the trigger will be a hydron.

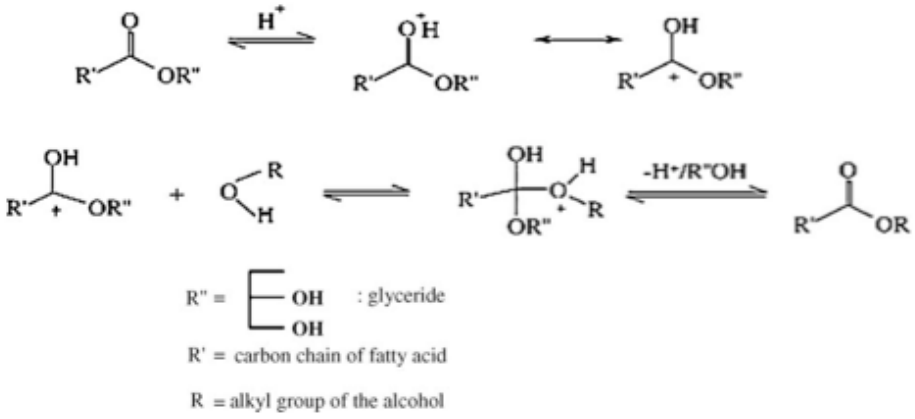


*Figure 1.4: Acid catalysed transesterification [10]*

In this case, the first step is the attack of the hydron of the acid on the carbonyl carbon atom, forming the tetrahedral intermediate. In the second step the alcohol will react with the intermediate, due to its negative charge. The last step is the rearrangement step, with the hydron of the catalyst being liberated again and the formation of the diglycerol and the ester.

### 3.2.4 Reaction conditions

Once the reaction is known, the conditions in which it happens should be determined. The parameters that will affect the reaction to a higher extent are: temperature, amount of alcohol, type and amount of catalyst, reaction time. Further, each of them will be discussed individually.

#### 3.2.4.1 Temperature

Temperature values for the transesterification reaction vary depending on the literature source. It is well known that higher temperatures speed up the reaction and shorten the reaction time. Apart from that, higher temperatures usually mean obtaining higher ester yields [11]. However; It should also be noted that if the reaction temperature is higher than the boiling point of the alcohol, it will evaporate, resulting in a lower yield [13]. It is also an accepted fact that usually the optimum temperatures for the transesterification range between 50 and 60ºC, depending on the kind of oil to be processed [14]. In the case of rapeseed oil, the optimum temperature value for its methanolysis has been found to be 65ºC [11].

#### 3.2.4.2 Reaction time

The reaction time clearly influences the outcome of the reaction, since the conversion rate increases with the reaction time [21]. If the reaction time is not long enough the ester yield will be low, therefore, part of the oil will be unreacted. For the rapeseed oil, when heat is used in the reaction, the optimum reaction time is two hours [11].

#### 3.2.4.3 Methanol/oil molar ratio

This is one of the most important factors that can affect the ester yield. It is related to the type of catalyst used, depending on that, the optimum value for the process can be obtained. Higher molar ratios give a higher ester yield in a shorter time. Usually, when using acid catalysts higher molar ratios are needed, probably because the use of acid catalysts is related to oils with high FFA content [21]. When rapeseed oil is transesterified using potassium hydroxide as a catalyst, the optimum molar ratio is 6:1.

#### 3.2.4.4 Catalyst concentration

This parameter is highly affected by the kind of catalyst used, different catalysts will require different concentrations. Even if they belong to the same group (as in the case of potassium hydroxide and sodium hydroxide), different concentrations will be necessary to attain the same yields. Therefore, the optimum value for every catalyst will have to be determined by titration. If the amount of catalyst is higher than the optimum, there will be a decrease in the yield of methyl esters due to the formation of soap in presence of high amount of catalysts, which apart from lowering the yield increases the viscosity of the reactants [11].

#### 3.2.4.5 Mixing

Mixing is mandatory for the reaction to take place. Without mixing, the reaction only occurs in the interface between the methanol and the oil and it is very slow to be viable. Therefore, a mixing device is needed in the reactor used for the process [11].

## 3.3 Cleaning raw biodiesel

When the transesterification reaction is finished, two products are obtained, biodiesel and glycerol. Both can be separated by sedimentation, since, due to their different densities, form two different liquid phases.

After the separation, raw biodiesel is obtained. This product still contains several different compounds that should be eliminated: residual catalyst, water, unreacted alcohol, free glycerol and soaps. Usually, before the cleaning step, methanol is removed using an alcohol stripper to prevent excess alcohol from entering the wastewater effluent in the case of the water cleaning and to follow the instructions marked by the producer when it comes to dry cleaning.

Both glycerol and alcohol can be easily removed by using water washing because they are highly soluble in water. By using water residual salts and soaps can also be eliminated. Water also helps to prevent the precipitation of saturated fatty acid esters and retards the formation of emulsions. Different stages have to be done to wash the biodiesel, which will

be washed when the water phase becomes clean. Afterwards, the water is separated from the biodiesel, they can be easily separated due to their density difference.

Dry washing consists of using different products which will substitute the water in order to remove impurities. In this case, the free glycerol level is reduced and soaps are also removed. The main advantage is the fact that no water is used, eliminating any problems with wastewater effluents. Among the different products that can be used, commercial brands such as Magnesol or D-Sol can be found. [14]

## 3.4 Characteristics of biodiesel

After the transesterification reaction and the cleaning, biodiesel is obtained. It is a clear amber-yellow liquid. Due to the conversion of triglycerides into esters, the molecular weight of biodiesel is one-third of the triglyceride, the viscosity is reduced by a factor of about eight and the volatility is also increased. This means that the viscosity of biodiesel is similar to the viscosity of diesel fuels. It should also be noted the fact that the esters of biodiesel contain 10-11% oxygen by weight, resulting in more combustion in an engine than hydrocarbon-based diesel fuels. The cetane number of biodiesel is around fifty.

Biodiesel is considered as a clean fuel because it has no sulphur or aromatics and its content in oxygen, which is helpful to burn it completely. Due to its higher cetane number it improves the ignition quality even if it is blended with mineral diesel. [10]

It has better lubricant properties than diesel fuel. It is also non-toxic and biodegrades quickly. The associated risk of handling, transporting and storing biodiesel is lower than that of mineral diesel. [3]

Table 3.4 shows a comparison of different fuel properties of petrodiesel and biodiesel:

| Fuel Property | Test method | ASTM D975 (Diesel) | ASTM D6715 (Biodiesel) |
|---|---|---|---|
| Flash point | D 93 | 325 K min | 403 K |
| Water and sediment | D 2709 | 0,05 max %vol | 0,05 max %vol |
| Kinematic viscosity (at 313 K) | D 445 | 1,3-4,1 mm2/s | 1,9-6,0 mm2/s |
| Sulphated ash | D 874 | - | 0,02 max %wt |
| Ash | D 482 | 0,01 max %wt | - |
| Sulphur | D 5453 | 0,05 max %wt | - |
| Sulphur | D 2622/129 | - | 0,05 max %wt |
| Copper strip corrosion | D 130 | No 3 max | No 3 max |
| Cetane number | D 613 | 40 min | 47 min |
| Aromaticity | D 1319 | 35 max %vol | - |

| Fuel Property | Test method | ASTM D975 (Diesel) | ASTM D6715 (Biodiesel) |
|---|---|---|---|
| Carbon residue | D 4530 | - | 0,05 max %mass |
| Carbon residue | D 524 | 0,35 max %mass | - |
| Distillation temp (90% volume recycle) | D 1160 | 555 K min-611 K max | |

*Table 3.4: ASTM standards of biodiesel and petrodiesel fuels [3]*

More information about biodiesel standards can be found in the Annex II.

# 3.5 Advantages and disadvantages of biodiesel

As it has been mentioned above, biodiesel can be used as a substitute for mineral diesel. When using it, several different advantages and disadvantages can be found. In the lines below, those will be explained in detail.

### 3.5.1 Advantages of biodiesel

The advantages of using biodiesel can be divided into three categories:

#### 3.5.1.1 Economic impacts

- Sustainability: Biodiesel promotes sustainability because it is a renewable fuel, with no carbon dioxide emissions and that avoids the use of fossil fuels.
- Fuel diversity: It means more competition and, also, more options for the consumer, that way the quality of the products is enhanced and the prices are lower.
- Increased number of rural manufacturing jobs: In order to grow the seeds, produce the oil and then the biodiesel, several workers are needed. Usually, this will happen in rural areas, meaning that more jobs will be available in those areas.
- Increased income taxes: Biodiesel, as any other fuel, is charged with taxes by the government, which receive more income taxes if biodiesel is used.
- Increased investments in plant and equipment: For the production of biodiesel it is necessary to build production plants and buy equipment.
- Agricultural development: As in the case of the rural manufacturing jobs, since it is necessary to grow the seeds, this will mean that the agriculture in the area will develop.
- International competitiveness: While the petroleum reserves are concentrated in just a few countries, in every country of the world biodiesel can be produced. Due to this, many countries could be able to join the fuels market, which would make it more competitive.

- Reducing the dependency on imported petroleum: The reason is fundamentally the same as the stated above, biodiesel can be produced by any country and being a substitute for diesel, there will be a lower necessity to import it.
- Inherent lubricity: The esters forming biodiesel have been analysed and it has been found that they show good potential as base stock in biodegradable lubricant formation.
- Higher cetane number: As shown in Table 3.4, biodiesel has a higher cetane number than diesel. [22, 23, 24, 25]

#### 3.5.1.2 Environmental impacts

- Greenhouse gas reductions: Complete combustion of diesel fuel releases 3.11 kg of $CO_2$ per kilogram while biodiesel releases 2.86 kg. Moreover, the carbon dioxide released by petroleum diesel was fixed from the atmosphere during the formative years of the earth. On the other hand, carbon dioxide released by biodiesel was fixed by plants in a recent year and will be recycled by the next generation of crops. It has been calculated that for each kilogram of diesel not used an equivalent of 3.11 kg of $CO_2$, plus an additional 15-20% for reduced processing energy, is not released to the atmosphere.
- Biodegradability: Biodiesel is non toxic and degrades about four times faster than petrodiesel. This is enhanced by its oxygen content, higher than the oxygen content of mineral diesel. Data obtained from a study shows that after 28 days, biodiesel fuels were biodegraded from 77 to 89%, while diesel fuel was only 18% biodegraded. Table 3.5 shows biodegradability data of different fuels:

| Fuel sample | Degradation in 28 d (%) |
|---|---|
| Gasoline (91 octane) | 28 |
| Heavy fuel (Bunker C oil) | 11 |
| Refined rapeseed oil | 78 |
| Refined soybean oil | 76 |
| Rapeseed oil methyl ester | 88 |
| Sunflower seed oil methyl ester | 90 |

*Table 3.5: Biodegradability data of petroleum and biofuels [4]*

- Higher combustion efficiency: In the literature different studies can be found supporting that esters prepared from oils can replace diesel oil. Moreover, it is stated that, under favourable conditions, biodiesel exceeds the performance of diesel fuel.
- Improved land and water use: Using biodiesel encourages using land for vegetable crops and, also, sensible use of water.

- Carbon sequestration: As explained above, when biodiesel crops are grown, the plants fix carbon dioxide.
- Lower sulphur content: Biodiesel contains less sulphur than diesel, which means lower sulphur emissions.
- Lower aromatic content: As in the case of the sulphur, the aromatic content of biodiesel is lower than that of mineral diesel, leading to lower aromatic emissions.

| Emission type | Pure biodiesel B100 | 20% Biodiesel + 80% petrodiesel B20 |
|---|---|---|
| Total unburned hydrocarbons (HC) | -67 | -20 |
| Carbon monoxide | -48 | -12 |
| Particulate matter | -47 | -12 |
| NOx | +10 | +2 |
| Sulphates | -100 | -20 |
| Polycyclic aromatic hydrocarbons | -80 | -13 |

*Table 3.6: Average biodiesel emissions (%) compared to conventional diesel, according to EPA (2002).*

- Less toxicity: Biodiesel is non-toxic. [22, 23, 24, 25]

#### 3.5.1.3 Energy security

- Domestic targets: Using biodiesel helps achieve targets in domestic fuel production.
- Supply reliability: Since it can be produced locally, the reliability of the supply is higher than that of internationally obtained products.
- Higher flash point: It has a higher flash point than diesel and that makes it less dangerous because it evaporates with more difficulty.
- Reducing use of fossil fuels: Being a direct substitute of diesel, it reduces its use.
- Ready availability: Production of biodiesel takes the time necessary to grow the crop, make the oil and then the biodiesel. Even if it may take a year, compared to the time that it takes to produce diesel fuel, it is a short period. This means that it can be available in a short period of time.
- Renewability: Because of its origin, which is oil produced from a crop, it is renewable because this source can be restarted as many times as wanted. [22, 23, 24, 25]

### 3.5.2 Disadvantages of biodiesel

Even if biodiesel has several advantages, its use also implies some disadvantages that should be mentioned:

- Agricultural feedstock is needed to produce biodiesel and at some times its availability might be constrained due to its necessity to produce food. This may impose limits on the production of biodiesel.
- The kinematic viscosity of biodiesel is higher than that of diesel fuel. This affects fuel atomisation during injection and requires modified fuel injection systems.
- Biodiesel has high oxygen content, which, when combusted, produces higher $NO_x$ levels than the produced by mineral diesel.
- Oxidation of biodiesel happens more easily than oxidation of diesel, so, when it is stored for long periods some products that may be harmful to the vehicle components might be produced.
- Biodiesel is hygroscopic, it absorbs water easily. Water content of biodiesel is limited by the standards. Thus, contact of biodiesel with sources of humidity should be avoided.
- Partly due to its local and home production, the biodiesel produced may not comply with European or US standards and it may cause corrosion, fuel system blockage, seal failures, filter clogging and deposits at injection pumps.
- Its lower volumetric energy density means that more fuel needs to be transported for the same distance travelled when using biodiesel than when using diesel.
- It can cause dilution of engine lubricant oil, requiring more frequent oil change than in standard diesel-fuelled engines.
- A modified refuelling infrastructure is needed to handle biodiesel, which adds to its total cost. [10]

# 4 EXPERIMENTAL PROCEDURE

For the realisation of this thesis, several different laboratory procedures were carried out. In this section, all of them will be explained in detail. More information about the equipment used for the experimental procedure can be found in the Annex III.

## 4.1 Titration

Before starting the biodiesel production, a test has to be performed. This test is called titration and it is used to determine the amount of free fatty acids present in the oil. This is compulsory to determine the amount of catalyst needed for the reaction.

### 4.1.1 Equipment

The equipment needed for the titration is:

- Magnetic stirrer
- Burette
- Plastic and volumetric pipettes
- Pipette bulb
- Volumetric flask
- Weight balance
- Erlenmeyer flask

### 4.1.2 Reagents

The following reagents are needed to perform the titration:

- Water
- Potassium or sodium hydroxide
- Phenolphthalein
- Isopropyl alcohol
- Vegetable oil

### 4.1.3 Procedure

The first step to take will be preparing the standard solution that will be used for the titration. The standard solution consists of 1 gram of catalyst (potassium or sodium hydroxide) diluted in 1 litre of water. To do so, 1 gram of catalyst is weighed in the balance, then diluted with water. This liquid is then poured in a volumetric flask and water is added till the volume is one litre.

Once the standard solution is ready, the titration itself can be performed. To do so, a burette filled with the standard solution has to be prepared. On the other hand, an Erlenmeyer flask with 10 mL of isopropyl alcohol and three drops of phenolphthalein has to be set. Then, it will be put on the magnetic stirrer. Standard solution is added till the solution turns pink, at that point the volume of standard solution is written down. Next, 1 mL of oil is incorporated and standard solution is added again till the solution turns pink. The new volume of standard solution is noted. The difference between the second and first volume is the amount of catalyst that has to be added apart from the 9 grams that are the base amount.

The calculations for that are as follows:

**x mL** of KOH standard solution for **1 mL** of vegetable oil

**x L** of standard solution for **1 L** of vegetable oil

**x L** of standard solution contains **x g** of KOH

From there, the amount that has to be added for the transesterification is calculated as:

**9 + x g** per litre of vegetable oil. [15]

## 4.2 Transesterification reaction

The transesterification reaction is the most important stage when producing biodiesel. Several different experiments were tried to find the most suitable procedure. First of all, the equipment and reagents needed will be explained. Afterwards, a description of the process will be given.

### 4.2.1 Equipment

The following equipment is needed for the transesterification reaction:

- Magnetic stirrer
- Volumetric pipette
- Pipette bulb
- Weight balance
- Erlenmeyer flask
- Graduated cylinder

### 4.2.2 Reagents

Several different kinds of catalysts, oils and alcohols can be used for the transesterification reaction, however, the ones used for the realisation of this paper are:

- Rapeseed, sunflower, linseed and hemp oils.
- Methanol
- Potassium hydroxide, sodium hydroxide and sulphuric acid.

### 4.2.3 Procedure

Several different procedures were tried to produce biodiesel. Many differences can be found among them. In the next sections all of them will be explained thoroughly.

#### 4.2.3.1 Amount and type of catalyst

Since alkali catalysts are the most suitable for this reaction, they were chosen to perform the transesterification. However, a choice between potassium and sodium hydroxide had to be done. Moreover, the exact amount of catalyst to be used had to be determined. This is so, because, even if the transesterification is supposed to give the amount of catalyst needed, it was found that using that quantity the reaction was incomplete.

To establish those parameters, the methodology used was very simple. Fixed amounts of rapeseed oil and methanol were used, 500 mL for the rapeseed oil and 100 mL for the methanol, while the amount and type of catalyst was varied. The amounts of both potassium and sodium hydroxide in the first trials were the obtained on the transesterification. Afterwards, lower and higher amounts were tried.

The first step before starting the reaction was mixing the catalyst and the alcohol, using the stirrer. Afterwards, this compound, called methoxide, was combined with the oil, using stirring again during the whole reaction period. The reaction time was set to 5 hours and the temperature that of the room, which was 21 ºC approximately. This means that no heat was used.

#### 4.2.3.2 Amount of methanol

This case was an attempt to determine whether or not it was possible to use reduced amounts of methanol for the reaction. Therefore, the amount of methanol was the only changing factor while all the others were kept constant. Lower values than 100 mL were tried. The conditions used were 6.8 grams of potassium hydroxide, 500 mL rapeseed oil, 5 hours as reaction time, continuous stirring and room temperature. Once again, the potassium methoxide was prepared before the actual reaction started and then it was added to the oil.

#### 4.2.3.3 Reaction temperature

Despite the fact that the purpose of the thesis is using no heat for the transesterification reaction, some trials were carried out using heat to compare the final results of both

options. Both 40 and 60 ºC were tried. Apart from that, the reaction was also tried at a temperature lower than room temperature, approximately 2 or 3 ºC.

The factors used, were 500 mL rapeseed oil, 100 mL of methanol and 6.8 grams of potassium hydroxide. The stirring was continuous in the case of the reactions at 40 and 60 ºC and the reaction time was 5 hours. However, due to some technical difficulties, that was not possible for the low temperature trial, therefore, the stirring was done in the next way: 30 minutes stirring, 50 minutes without stirring, 10 minutes stirring, 50 minutes without it. The last part, the 10-50, was repeated until the reaction time was 5 hours. As in all the previous cases, the methoxide was prepared first and then it was added to the oil.

#### 4.2.3.4 Way of adding the catalyst

As stated above, the common method consists of preparing the methoxide before mixing it with the oil. However, there was not a convincing reason for this. Consequently, an experiment in which the methanol and the potassium hydroxide were added without being previously mixed was attempted.

The conditions were 500 mL rapeseed oil, 100 mL methanol, 6.8 grams of potassium hydroxide, 6 hours reaction time, room temperature and continuous stirring. The methanol and the potassium hydroxide were added to the rapeseed oil at the same time, without previous mixing.

Another way of adding the catalyst was also tried, in this case, the potassium hydroxide and the methanol were mixed to form the potassium methoxide before adding it to the oil, but not all the methoxide was added at the beginning, just two-thirds of it. The other third was added after some reaction time had taken place and the glycerol obtained had been separated. This was an endeavour to see if the catalyst amount could be reduced.

Two different amounts of catalyst were tried, 6.2 and 6.8 grams of potassium hydroxide. As in the previous cases, 500 mL of oil and 100 mL of methanol were used, as well as continuous stirring and room temperature. As explained above, the methoxide was prepared and just two-thirds (by volume) were added at the beginning. After two hours, the reaction was stopped and the products were poured into a separatory funnel, where they stayed for half an hour, enough time for the two phases to separate. When the time had passed, the glycerol was extracted, the biodiesel was set on the stirrer again and the rest of the methoxide was added. Two extra hours were necessary to complete the reaction.

#### 4.2.3.5 Stirring

Stirring is mandatory for this reaction to start, because, without stirring, reaction only happens in the interface, which goes to a very low extent. Therefore, stirring is needed, at least, in the beginning, if not during the whole reaction time. To determine if continuous stirring is necessary, an experiment was made, using the same stirring times as in the case of the cold temperature, that is, 30 minutes stirring, 50 minutes without stirring, 10 minutes stirring, 50 minutes without stirring and repeating this last period until the reaction time was 5 hours.

The rest of the setup was 500 mL rapeseed oil, 100 mL methanol, 6.8 grams of KOH and the methoxide was first produced and then added to the rapeseed oil.

#### 4.2.3.6 Type of oil

The reaction parameters were designed to be optimum for rapeseed oil, but it had to be proven that they would work with any other kind of oil as long as the amount of free fatty acids was not too elevated. To do so, samples of sunflower oil and linseed oil were tested. The reaction conditions were 500 mL of oil, 100 mL of methanol, 6.8 grams of potassium hydroxide, 5 hours reaction time, continuous stirring and room temperature.

#### 4.2.3.7 Acid catalyst

While alkali catalysts have a higher yield and shorter reaction times, they are not recommended when the content of free fatty acids in the oil is too high (usually when the value obtained in the titration is higher than 3). In this cases, an acid catalyst, sulphuric acid with a purity of 98%, is used.

The first part of this process is different from the process used for the alkali catalyst. Initially, the amount of acid has to be calculated, it is done with this formula:

*Millilitres of $H_2SO_4$ per litre of oil = (Initial Titration - Target Titration) * 0.2* [26]

Since the alkali method is recommended for titration values lower than three, the target titration was set in that value. Once the millilitres of sulphuric acid were calculated, the reaction could be started. As previously, the acid was first mixed with the methanol and then added to the oil. However, there are some differences in this method, because in the first part only 50 mL of methanol were added and the reaction time was approximately one day (it was always left overnight). Apart from that, the other factors were maintained in the same way, 500 mL of oil, continuous stirring and room temperature were used.

After the first part of the reaction, the liquid was poured into a separatory funnel, where the water remanent was extracted. Afterwards, a titration was made to determine

whether the amount of free fatty acids was correct and then the alkali reaction was started. This process was done twice with different oils, old rapeseed oil and hemp oil. For the hemp oil, which gave the highest titration amount, 100 mL of methanol were used in the alkali part. On the other hand, for the old rapeseed oil, only 50 mL were used. Besides, the amount of catalyst was the obtained in the titration, the reaction time was 5 hours, continuous stirring was used and it was done at room temperature. As in the other cases, the potassium methoxide was first mixed and then it was added to the oil. [15, 26]

## 4.3 Separation of the products

### 4.3.1Equipment

The only piece of equipment which is needed for the separation of glycerol and biodiesel is a separatory funnel.

### 4.3.2 Procedure

The liquid product obtained from the transesterification reaction, which was basically formed by glycerol and biodiesel, is placed in the separatory funnel. It stays there overnight (around 18 hours) and then, the glycerol, which is the heaviest product, is separated because it forms the phase which stays in the bottom.

## 4.4 Cleaning biodiesel with water bubbling

### 4.4.1 Equipment

- Separatory funnel
- Air flow machine (more information about this can be found in the Annex IV)

### 4.4.2 Reagents

- Raw biodiesel
- Water

### 4.4.3 Procedure

The raw biodiesel which is obtained after the separation from the glycerol needs to be cleaned. One of the possibilities to achieve the cleaning is using water and bubbling air through it. This will dissolve the soap, unreacted oil and other impurities which can be found in the raw biodiesel.

The steps to follow are not complicated. Usually, three different cleaning stages are done. The first and the last are short, about one hour, and the intermediate is long, more

than one day. The water volume needed for every step is approximately the same as the biodiesel volume.

The process starts by putting the biodiesel in the separatory funnel, then, the water is added carefully. Next, the air bubbling is set and started. It is important that the bubbles are not too big or too fast, this may create an emulsion between the water and the biodiesel and the biodiesel might not be recovered. To set the air bubbling, a hose is introduced in the lowest part of the separatory funnel. After the stage time, the bubbling is stopped, the liquids are left to settle for about half an hour and then the water is extracted. Afterwards, either a new stage is started or the biodiesel is already prepared to be used. It should be noted that it is important for the water after the last stage to be clean, which means that all the impurities have already been eliminated. It is also recommended, for that reason, the longest stage not to be the last, because it is in that stage when the majority of the impurities are removed and the water will not be clear after that.

## 4.5 Cleaning biodiesel with dry products

### 4.5.1 Equipment

- Weight balance
- Magnetic stirrer
- Erlenmeyer flask
- Büchner funnel with elastomer adapter
- Kitasato flask
- Hose
- Vacuum pump
- Filter paper

### 4.5.2 Reagents

Several different cleaning agents were tried, more information about them can be found in the Annex V.

- Magnesol
- D-Sol
- Aerogel
- Raw biodiesel

### 4.5.3 Procedure

The first step to take is to weigh the amount of drying product needed. This will vary depending on the using instructions provided by the manufacturer. In the case of the D-Sol it is 0.5% in weight, while for aerogel and magnesol it is 1.5%, also in weight. All the products are powder like solids. Oil is added till the 100% in weight value is achieved and then the mixture is stirred for twenty minutes. After that time, a vacuum filtration is done, using the Büchner funnel, the Kitasato flask and filter paper. The filtration is done twice, using the same paper where a cake of powder has been created, which, once created, will act as the filtering medium. When the second stage of the filtration is finished, the biodiesel is cleaned and ready to be used.

## 4.6 3/27 test

### 4.6.1 Equipment

- Pipettes
- Pipette bulb
- Test tubes

### 4.6.2 Reagents

- Methanol
- Raw biodiesel

### 4.6.3 Procedure

The 3/27 test, also called Jan Warnquist test after its developer, is used to find the degree in which triglycerides are converted into methyl esters in the transesterification reaction. Therefore, with this test, the development of the reaction can be known. To perform the test, methanol and raw biodiesel are needed. First, 27 parts of methanol are put into a test tube. Afterwards, three parts of raw biodiesel are added and the content of the tube is agitated. After a resting period of 30 minutes, it can be checked whether any precipitate has appeared, if there is precipitate the test has not been passed, meaning that the reaction is not complete. If the test is performed properly, and a batch of fuel passes, (there is no visible precipitate) then the fuel is likely to be converted very close to the ASTM standard for conversion of 0.24% total glycerides or better. [27]

## 4.7 Solubility test

### 4.7.1 Equipment

- Pipettes
- Pipette bulb
- Test tubes

### 4.7.2 Reagents

- Raw biodiesel
- Water

### 4.7.3 Procedure

Methyl esters, as well as vegetable oil, are not miscible with water. Therefore, a good quality biodiesel should have a low solubility in water, which indicates that not many impurities are present. To prove so, a simple test was performed, which consisted of mixing one volume of raw biodiesel with one volume of water in a test tube. After shaking the tube, it was allowed to settle for half an hour. Then, the extent to which biodiesel is dissolved in water, the turbidity of biodiesel due to water and the amount of soap in the interface could easily be seen with a naked eye.

## 4.8 Soap test

### 4.8.1 Equipment

- Erlenmeyer flask
- Pipettes
- Pipette bulb
- Burette
- Magnetic stirrer
- Balance

### 4.8.2 Reagents

- Isopropyl alcohol
- Phenolphthalein
- 0.01 N HCl
- 0.04% Bromophenol blue in water
- Biodiesel

### 4.8.3 Procedure

The soap test is used to determine the amount of soap in raw biodiesel. With it, the quantity of dry cleaning product can be determined. It is also useful to know the quality of the obtained biodiesel.

The grams of soap in a gram of biodiesel can be determined with the formula shown in figure 4.1.

$$Grams\ of\ soap\ /\ gram\ of\ sample = \frac{B \cdot 0.1 \frac{mol\ HCl}{l} \cdot 320.56 \frac{g}{mol\ soap}}{1000 \cdot W}$$

$$B = mL\ 0.01\ N\ HCl$$

$$W = g\ biodiesel$$

*Figure 4.1: Calculation of the amount of soap in a biodiesel sample [28]*

The procedure of the test starts with the preparation of an Erlenmeyer flask with 100 mL of isopropyl acid and 5 drops of phenolphthalein. Then, ten grams of biodiesel are added. If the mixture turns pink, it means that there is some unreacted catalyst in the raw biodiesel. In that case, 0.01N HCl has to be added till the pink colour disappears. In the case it doesn't, that step is skipped and the next is started. In the next step, 18 drops of bromophenol blue are added to the mixture and then it is weighed. The colour of the liquid will now be blue. After this, HCl, which is contained in a burette, is incorporated while stirring until the colour turns yellow. The Erlenmeyer flask is weighed again and the volume of HCl used is noted. [28]

## 4.9 Using the centrifuge

### 4.9.1 Equipment

The centrifuge is the most important piece of equipment needed in this part of the experimental procedure. More information about it and about the AC drive can be found in the Annex VI.

- Centrifuge
- AC drive
- Funnel
- Tube

### 4.9.2 Reagents

- Biodiesel
- Oil

- Glycerol
- Water

### 4.9.3 Procedure

The purpose of using the centrifuge was to find out whether or not it can be used for the separation of different liquids and mixtures of liquids that are often found when making biodiesel. In this case, the centrifuge was connected to an AC Drive, allowing it to reach 6000 rpm.

The procedure was very simple, the first step was to switch on the centrifuge and set it to the maximum speed. Afterwards, the liquid that had to be purified or separated was added to the centrifuge using a funnel that was connected with a tube. When the centrifuge was full enough, the lightest liquid would leave by one of the sides while the heaviest compounds stayed inside the centrifuge until it was stopped.

# 5 RESULTS

## 5.1 Titration

Prior to the transesterification reaction, the titration of the oils should be done to calculate the amount of catalyst which is necessary. During the lab trials, titrations with both potassium hydroxide and sodium hydroxide were done, the results of both of them are shown in table 5.1 and table 5.2.

| Type of oil | Volume of 1g/L KOH (mL) | Grams of KOH/L of oil | Grams of KOH/500 mL of oil |
|---|---|---|---|
| Rapeseed 1 | 7.7 | 16.7 | 8.4 |
| Rapeseed 2 | 4.1 | 13.1 | 6.6 |
| Rapeseed 3 | 3.5 | 12.5 | 6.3 |
| Sunflower | 1.7 | 10.7 | 5.4 |
| Hemp | 18.3 | 27.3 | 13.7 |
| Linseed | 3.3 | 12.3 | 6.2 |

*Table 5.1: Titration results when using KOH as a catalyst*

| Type of oil | Volume of 1g/L NaOH (mL) | Grams of NaOH/L of oil | Grams of NaOH/500 mL of oil |
|---|---|---|---|
| Rapeseed 2 | 2.8 | 6.3 | 3.2 |

*Table 5.2: Titration results when using NaOH as a catalyst*

Table 5.1 shows the results obtained when using potassium hydroxide as a catalyst, while table 5.2 is for the sodium hydroxide. In the first case three different types of rapeseed oil were tested and the second type was the one chosen to be the raw oil for all the experiments when rapeseed oil was used as a reagent. The grams of catalyst for 500 mL of oil are shown because this is the volume of oil that was used in all the experiments.

The difference between the three types of rapeseed oil is basically, that they were stored in different containers and they had been obtained at different dates, so, the titration for the three of them had to be done.

## 5.2 Biodiesel production

### 5.2.1 Influence of the catalyst

As it has been previously explained, the catalyst is one of the most important factors affecting the reaction. The next sections will show the influence of different catalysts and the way of using them when doing the transesterification reaction. All the reactions were done at room temperature, which was approximately 21 ºC.

### 5.2.1.1 Amount of potassium hydroxide

| Sample | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.7 | 500 | 100 | 5 | 92 | 93.7 | 480 | 415.9 | Not passed |
| 2 | 6.2 | 500 | 100 | 5 | 92 | 91.3 | 495 | 425.6 | Not passed |
| 3 | 6.8 | 500 | 100 | 5 | 94 | 96.9 | 490 | 421.9 | Passed |
| 4 | 7.5 | 500 | 100 | 5 | 92 | 95.1 | 475 | 409.7 | Passed |
| 5 | 7.8 | 500 | 100 | 5 | 103 | 105.1 | 475 | 419.3 | Passed |

*Table 5.3: Influence of the amount of potassium hydroxide in the production of biodiesel*

Five different amounts of potassium hydroxide were tried, in all the cases the rest of factors were the same. In table 5.3 it can be seen that only three out of five experiments were successful, that is, passed the 3:27 test. This indicates that a minimum amount of 6.8 grams of KOH is necessary to obtain a complete reaction. Therefore, that amount was decided to be the standard amount of potassium hydroxide when doing the transesterification reaction with the sample 2 of rapeseed oil.

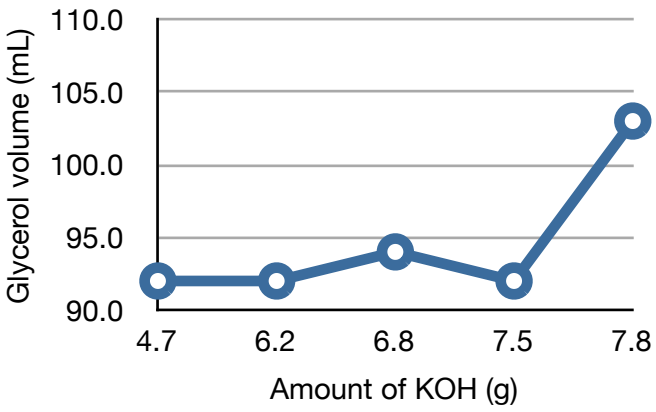


*Figure 5.1: Variation of the volume of glycerol produced depending on the amount of KOH*

The volume of glycerol produced increases highly with the amount of catalyst used.

### 5.2.1.2 Amount of sodium hydroxide

| Sample | Amount of NaOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3.2 | 500 | 100 | 5 | 79 | 80.4 | 485 | 418.8 | Not passed |
| 2 | 3.5 | 500 | 100 | 5 | 86 | 88.4 | 470 | 410.8 | Not passed |
| 3 | 4.0 | 500 | 100 | 5 | 90 | 85.9 | 480 | 414.7 | Passed |

*Table 5.4: Influence of the amount of sodium hydroxide in the production of biodiesel*

As in the previous case, different amounts were tested. When using sodium hydroxide as a catalyst, only one of the samples passed the 3:27 test. In the other cases, the reaction was not complete.

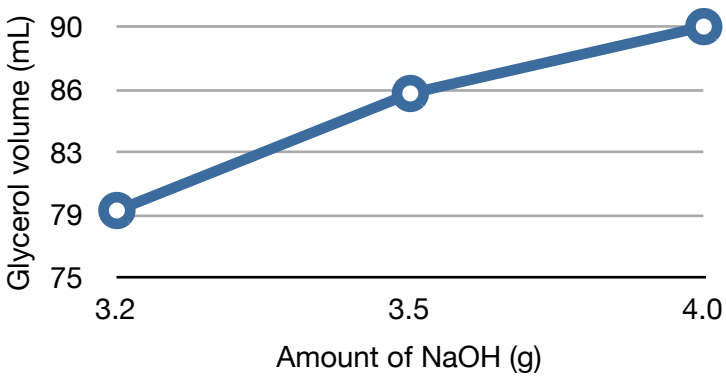


*Figure 5.2: Variation of the volume of glycerol produced depending on the amount of NaOH*

The higher the amount of sodium hydroxide used in the transesterification reaction, the higher the volume of glycerol produced, that can also mean a lower biodiesel yield.

#### 5.2.1.3 Not preparing the potassium methoxide previously

To find out whether it was possible to do the transesterification reaction without preparing the methoxide previously, this was tried in one of the experiments, at room temperature. The results of the experiments are displayed in table 5.5.

| Sample | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 6.8 | 500 | 100 | 6 | 93 | 96.8 | 480 | 419.8 | Passed |

*Table 5.5: Results obtained when the potassium methoxide was not previously mixed*

The reaction time is longer than usual due to some mixing difficulties that were observed at the beginning of the reaction.

#### 5.2.1.4 Adding the potassium hydroxide in two stages

As an attempt to save catalyst, the two-thirds method was tried at room temperature. Two different amounts of catalyst were tried, 6.2 and 6.8 grams.

| Sample | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 6.2 | 500 | 100 | 4 | 80 | 85.1 | 490 | 425.6 | Passed |
| 2 | 6.8 | 500 | 100 | 4 | 90 | 95.2 | 485 | 417.6 | Passed |

*Table 5.6: Results obtained when adding the potassium methoxide in two stages*

| Sample | Stage 1 | | | | Stage 2 | | | |
|---|---|---|---|---|---|---|---|---|
| | $V_{methoxide}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{methoxide}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) |
| 1 | 66 | 2 | 56 | 60 | 34 | 2 | 24 | 25.1 |
| 2 | 66 | 2 | 61 | 64.1 | 34 | 2 | 29 | 31.1 |

*Table 5.7: Volumes and masses of glycerol obtained*

Both experiments were successful. The reaction time was a bit shorter than usual because there was some sedimentation time between both reaction stages and it was considered that four hours would be enough. It should also be mentioned that the result of the solubility test was much worse than the result obtained when preparing the potassium hydroxide previously.

#### 5.2.1.5 Two stage acid-alkali reaction

When the amount of free fatty acids is too high, a two stage reaction is recommended. First, an acid catalyst is used and then an alkali catalyst. This was done with two different kinds of oils, one type of rapeseed oil and hemp oil. The titration results for them were 16.7 and 27.3 grams of potassium hydroxide per litre of oil, respectively.

| Sample | Type of oil | $V_{H2SO4}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | Titration result (mL) |
|---|---|---|---|---|---|
| 1 | Hemp | 3 | 50 | 23 | 3.0 |
| 2 | Rapeseed 1 | 1 | 50 | 23 | 1.2 |

*Table 5.8: Results of the acid catalised reactions*

After the reaction, which was done overnight with continuous stirring and at room temperature, the titration of the products was done, obtaining low amounts of potassium hydroxide. Therefore, the alkali catalysed reaction could be done. The results of the second stage are shown in table 5.9.

| Sample | Type of oil | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Hemp | 6 | 500 | 100 | 5 | 116 | 123.3 | 462 | 405.2 | Passed |
| 2 | Rapeseed 1 | 5.1 | 500 | 50 | 5 | 100 | 100.8 | 410 | 361.3 | Not passed |

*Table 5.9: Results obtained in the second stage of the acid-alkali catalysed reactions*

In this case, there was an important difference between the two reactions, in the case of hemp oil, 100 mL of methanol were used in the second stage, while only 50 mL were used with the rapeseed oil. This was done to try whether or not it was possible to use only 50 mL in the second stage because 50 more had already been used in the first one. As it can be seen in the results, the product obtained from the rapeseed reaction is not completely transesterified.

### 5.2.2 Influence of methanol

Methanol, with oil, is one of the reagents of the transesterification. The amount of methanol used will lead to high variations in the results of the reaction. Moreover, saving methanol means lower costs when producing biodiesel. Different amounts were tried to find out the best option. All the reactions were done at room temperature.

| Sample | Amount of methanol (mL) | $V_{oil}$ (mL) | $M_{KOH}$ (g) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 60 | 500 | 6.8 | 5 | 104 | 103.7 | 420 | 372.1 | Not passed |
| 2 | 80 | 500 | 6.8 | 5 | 98 | 100.6 | 465 | 403.9 | Not passed |
| 3 | 100 | 500 | 6.8 | 5 | 94 | 96.9 | 490 | 421.9 | Passed |

*Table 5.10: Influence of the amount of methanol in the production of biodiesel*

Only when 100 mL of methanol was used, that is, 20% of the amount of rapeseed oil, the reaction was complete. Furthermore, with low quantities of methanol, the separation of the glycerol and biodiesel phases became complicated due to the high viscosity of the glycerol.

There is another important factor in this case, the production of biodiesel. It can be seen from the data that the yield of biodiesel decreases when the volume of methanol is lower.

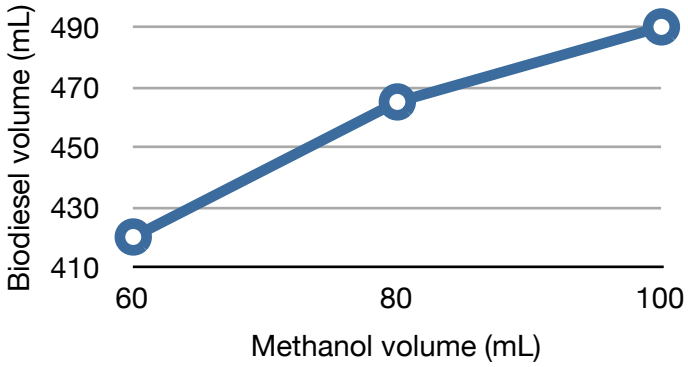


*Figure 5.3: Variation of the volume of biodiesel produced depending on the amount of methanol*

A higher methanol volume in the transesterification reaction gives a higher biodiesel yield, as it can be seen in figure 5.3.

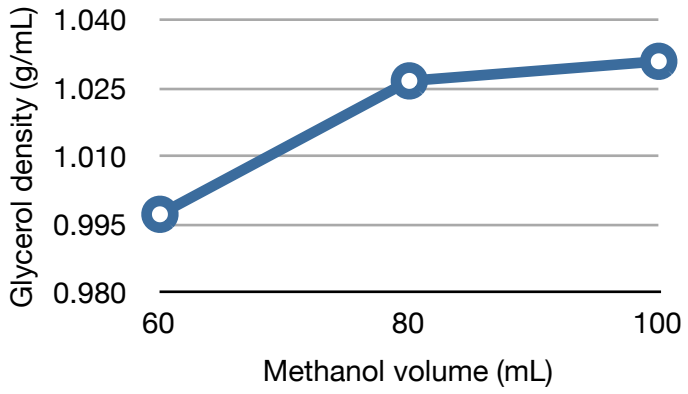


*Figure 5.4: Variation of the density of glycerol depending on the volume of methanol*

Finally, there is another important factor, the density of glycerol, that should not be forgotten. The density is higher when higher amounts of methanol are used because the separation of the phases is better, since less biodiesel is dissolved in the glycerol phase.

### 5.2.3 Influence of the temperature

Since the objective of this thesis is to find a suitable method to produce biodiesel without using a heat source, different reactions using heat were done to compare the results of both options. In this part, the results of those reactions are shown.

| Sample | T (ºC) | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 21 (room T) | 6.8 | 500 | 100 | 5 | 94 | 96.9 | 490 | 421.9 | Passed |
| 2 | 40 | 6.8 | 500 | 100 | 5 | 106 | 108.3 | 460 | 397.5 | Passed |
| 3 | 60 | 6.8 | 500 | 100 | 5 | 132 | 132.8 | 395 | 344.1 | Passed |

*Table 5.11: Influence of the temperature on the transesterification reaction*

First of all, it should be mentioned that all the trials passed the 3:27 test, therefore, the oil was fully reacted in all the cases. The results show clearly the difference in the yield of biodiesel with the temperature when long reaction times ares used. With higher temperature, higher glycerol yields and lower biodiesel yields are obtained.

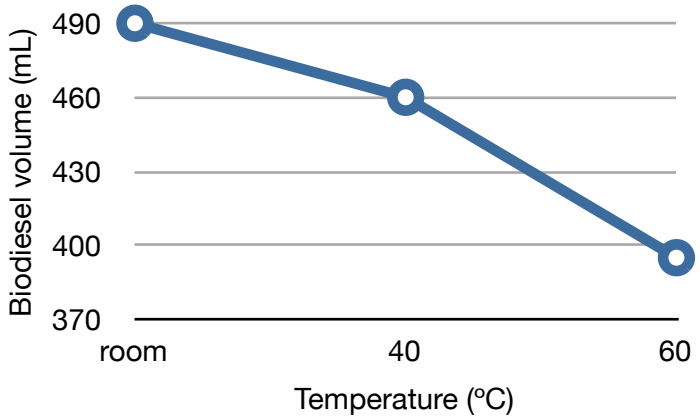


*Figure 5.5: Evolution of the volume of biodiesel with the temperature*

In this experiment, the results of the solubility test have certain importance too. Those results were better when the temperature was lower.

Since the amount of glycerol obtained at 60ºC was found to be too high, a new reaction was started, with the difference, that, in this case, the reaction time was set to just an hour.

| Sample | T (ºC) | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 60 | 6.8 | 500 | 100 | 1 | 83 | 87.1 | 480 | 419.8 | Passed |

*Table 5.12: Biodiesel production at 60ºC after 1 hour*

The 3:27 test was passed, which indicates that the reaction was complete.

Another trial was done at low temperatures. Due to technical difficulties (it had to be done outside), stirring could only be done for half an hour at the beginning of the reaction and, then, for ten minutes in every hour. Since the results of this experiments could not be compared with those of a reaction at room temperature with continuous stirring, a trial at room temperature with the same stirring times was done. The results of both tests are shown in table 5.13.

| Sample | T (ºC) | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 6.8 | 500 | 100 | 5.5 | 86 | 89.1 | 500 | 430.4 | Not passed |
| 2 | 21 (room T) | 6.8 | 500 | 100 | 5.5 | 93 | 96.1 | 460 | 397.1 | Passed |

*Table 5.13: Results of the experiments at low temperature*

When the trial was done outside, at about 3ºC, the reaction was not complete because the 3:27 test was not passed. However, the biodiesel obtained at room temperature passed the test. The reaction time was longer than usual in an attempt to minimise the effect of the short stirring time. It should be mentioned that the volume of biodiesel obtained in the room temperature trial was higher than 460 mL, but, due to some spilling, part of it was lost.

### 5.2.4 Experiments with different kinds of oils

To prove the validity of the method to produce biodiesel at room temperature, it was also tried using other oils apart from rapeseed oil. Hemp was tried in the acid-alkali method, while, sunflower and linseed were used with alkali catalysts.

| Sample | Type of oil | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Linseed | 6.8 | 500 | 100 | 5 | 76 | 81.4 | 495 | 427.4 | Passed |
| 2 | Sunflower | 5.4 | 500 | 100 | 5 | 87 | 92.2 | 495 | 436.9 | Passed |

*Table 5.14: Results of the transesterification reaction with linseed and sunflower oils*

Both experiments were successful, with slight differences in the amount of glycerol obtained. This could be due to the differences of viscosity and properties of the oils.

## 5.3 Soap titration

Soap tests were performed for the biodiesel samples that passed the 3:27 test and were found to be significative due to different factors. The result of those tests is shown in the table below. As mentioned in the experimental procedure, the quantity of soap in the biodiesel was calculated with the formula shown in figure 5.6.

$$Grams\ of\ soap\ /\ gram\ of\ sample = \frac{B \cdot 0.1 \frac{mol\ HCl}{l} \cdot 320.56 \frac{g}{mol\ soap}}{1000 \cdot W}$$

$$B = mL\ 0.01\ N\ HCl$$

$$W = g\ biodiesel$$

*Figure 5.6: Calculation of the grams of soap per gram of biodiesel [28]*

| Sample | $V_{HCl\ 0.01\ N}$ (mL) | Biodiesel sample (g) | Soap/biodiesel (g/g) |
|---|---|---|---|
| **Room T** | 2.2 | 10 | 0.007 |
| **40 ºC** | 2.2 | 10 | 0.007 |
| **60 ºC** | 5.5 | 10 | 0.018 |
| **60 ºC (1h)** | 4.1 | 10 | 0.013 |
| **2/3 (6.2 g KOH)** | 6.9 | 10 | 0.022 |
| **2/3 (6.8 g KOH)** | 5.5 | 10 | 0.018 |
| **Sunflower** | 3.2 | 10 | 0.010 |
| **Linseed** | 2.9 | 10 | 0.009 |
| **Hemp** | 3.8 | 10 | 0.012 |

*Table 5.15: Soap content of different biodiesel samples*

The soap content varies widely depending on how the biodiesel was done, that is, depending on the conditions of the reaction and, also, on the oil used to make biodiesel.

## 5.4 Cleaning biodiesel

In order to try the different biodiesel cleaning options, several biodiesel batches were prepared, using the conditions that were found to be the best after all the experiments that had been performed before. The data about those batches can be seen in table 5.16.

| Sample | Amount of KOH (g) | $V_{oil}$ (mL) | $V_{methanol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) | 3:27 test |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 6.8 | 500 | 100 | 5 | 98 | 100.3 | 480 | 413.2 | Passed |
| **2** | 6.8 | 500 | 100 | 5 | 94 | 96.9 | 490 | 421.9 | Passed |
| **3** | 6.8 | 500 | 100 | 5 | 92 | 96.5 | 490 | 424.2 | Passed |
| **4** | 6.8 | 500 | 100 | 5 | 91 | 95.0 | 485 | 423.2 | Passed |
| **5** | 6.8 | 500 | 100 | 5 | 93 | 96.3 | 480 | 414.3 | Passed |
| **6** | 6.8 | 500 | 100 | 5 | 99 | 101.8 | 460 | 406.3 | Passed |
| **7** | 6.8 | 500 | 100 | 5 | 99 | 101.3 | 460 | 403.9 | Passed |
| **8** | 6.8 | 500 | 100 | 5 | 94 | 96.9 | 480 | 413.9 | Passed |

*Table 5.16: Biodiesel batches for cleaning*

Soap titrations were done both before and after the cleaning. The results are presented separately, on the one hand the dry cleaning and on the other hand the water cleaning.

| Cleaning system | Amount of cleaning product (g) | Biodiesel (g) | Soap titration before (mL) | Soap/biodiesel before (g/g) | Soap titration after (mL) | Soap/biodiesel after (g/g) (mL) | % reduction |
|---|---|---|---|---|---|---|---|
| Magnesol 1 | 7.5 | 492.5 | 3.5 | 0.011 | 0.5 | 0.002 | 85.7 |
| Magnesol 2 | 7.5 | 492.5 | 5.5 | 0.018 | 1.8 | 0.006 | 67.3 |
| D-Sol | 2.5 | 497.5 | 3.5 | 0.011 | 1.1 | 0.004 | 68.6 |
| Aerogel 250 | 7.5 | 492.5 | 3.5 | 0.011 | 0.7 | 0.002 | 80.0 |
| Aerogel | 7.5 | 492.5 | 3.5 | 0.011 | 0.8 | 0.003 | 77.1 |

*Table 5.17: Dry cleaning results*

Magnesol 1 and 2 refers to the same type of product, but, due to an error, in the first filtration two filter papers were used instead of one, so the experiment was repeated. Otherwise, Aerogel 250 and Aerogel are different products and more information about them can be found in the Annex V.

| Cleaning system | Number of stages | | Duration of stages (h) | | Soap titration before (mL) | Soap/biodiesel before (g/g) | Soap titration after (mL) | | Soap/biodiesel after (g/g) (mL) | | % reduction soap | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water bubbling | 3 | 4 | 1-3-1 | 1-3-1-94 | 5.5 | 0.018 | 3 | 4 | 3 | 4 | 3 | 4 |
| | | | | | | | 2.0 | 0.7 | 0.006 | 0.002 | 63.6 | 87.3 |
| Magnesol 1+ water bubbling | 3 | | 1-72-1 | | 5.5 | 0.018 | 0.1 | | 0.000 | | 98.2 | |

*Table 5.18: Water cleaning results*

For the first water cleaned sample, the soap titration was done twice, one after 5 hours of cleaning (3 changes of water) and the other after a new step which took 4 days. The biodiesel cleaned with Magnesol was also cleaned with water afterwards in three steps (1 hour, 72 hours, 1 hour).

## 5.5 Using the centrifuge

Six different tests were done using the centrifuge, some with just one component and others with two-phase liquids.

| Components | Composition | Result |
|---|---|---|
| Sunflower oil | - | Impurities were extractred |
| Biodiesel + glycerol | 50:50 | No separation of the liquids |
| Biodiesel + water | 90:10 | No separation of the liquids |
| Raw biodiesel | - | No impurities extracted |
| Raw rapeseed oil | - | No impurities extracted |
| Raw glycerol | - | No impurities extracted |

*Table 5.19: Using the centrifuge*

# 6 DISCUSSION

## 6.1 Titration

The results of the titration showed clear variations on the amounts of free fatty acids of the different oils. This may be caused by the composition of the oil, but also because of long storage times, which usually lead to decomposition of the triglycerides and, thus, more content of free fatty acids.

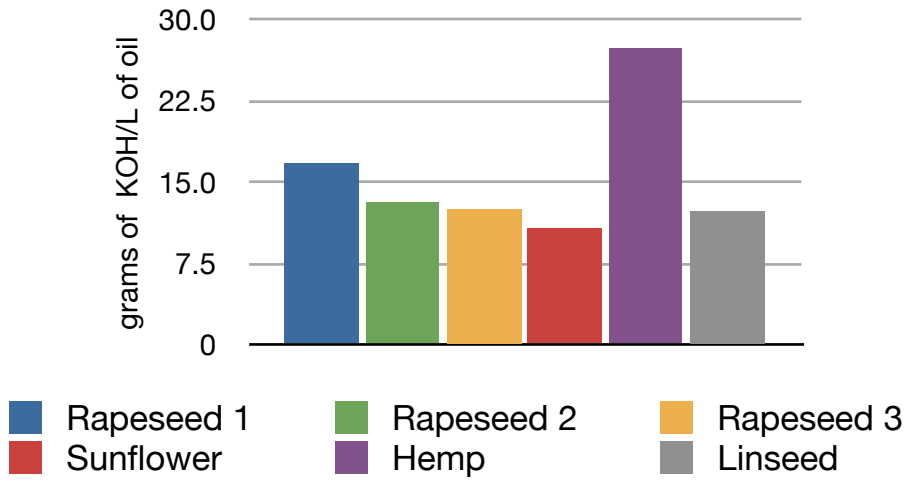


*Figure 6.1: Comparison of the titration results of the different oils*

## 6.2 Biodiesel production

### 6.2.1 Reaction time

Even if specific experiments to determine the most appropriate reaction time were not performed, it was determined that 5 hours was the best value for most of the reaction times. This is because it is enough time for the reaction to be complete. The only limitation imposed by the reaction time is that, in case it is not long enough, the reaction will not be complete. Therefore, allowing a long enough time will avoid any problems and ensure a complete reaction.

### 6.2.2 Influence of the catalyst

#### 6.2.2.1 Amount of potassium hydroxide

Several difficulties were found in the first attempts to obtain a fully reacted biodiesel. Therefore, five different amounts of catalyst were tried. This indicates that the titration results may not always be completely correct. However, it can be used as a starting point. Especially if large volumes of biodiesel are to be produced at a time, it is recommended to try the reaction parameters first with small batches to ensure the fully completion of the reaction. Another important factor is that the production of glycerol

increases with the amount of catalyst. Because of this, the biodiesel yield may be affected.

Obtaining a pass in the 3:27 test meant that the objective of this thesis was fulfilled, that is, biodiesel can be produced at room temperature. These first trials were helpful to determine important factors for the next experiment, like the reaction time, which was decided to be five hours, the continuous stirring and, of course, the amount of potassium hydroxide to use.

#### 6.2.2.2 Amount of sodium hydroxide

Sodium hydroxide, as well as potassium hydroxide, is one of the most widely used catalysts when producing biodiesel. Sodium hydroxide, compared to potassium hydroxide, means using lower amounts of catalyst. However, it is more difficult to dissolve because of its shape (potassium hydroxide is prepared as flakes, while sodium hydroxide is prepared as lentils) and it is also more expensive. Therefore, it was decided that potassium hydroxide would be the catalyst used for all the reactions.

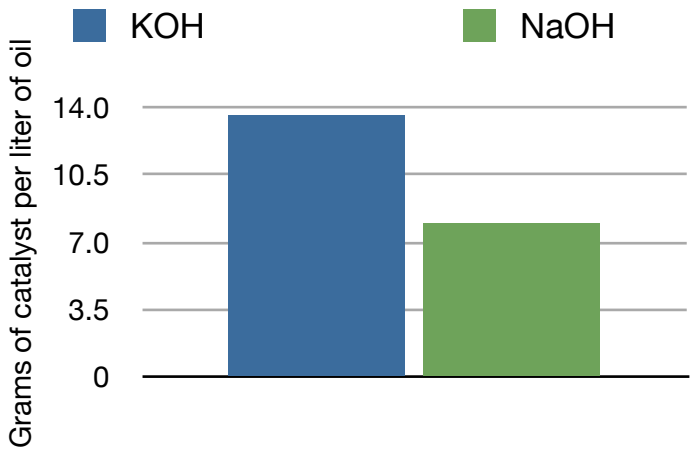


*Figure 6.2: Comparison between KOH and NaOH*

#### 6.2.2.3 Not preparing the potassium methoxide previously

Since the 3:27 test was passed, it can be said that there is not a necessity to prepare the methoxide previous to the transesterification reaction. However, it was also observed that it took longer to start the reaction in this case, because of the increased difficulty to dissolve the flakes of potassium hydroxide. This is why the reaction time chosen was longer than in the previous cases, to allow the reaction to be complete. It can be observed from the results that the products obtained are similar to what is obtained with previous mixing.

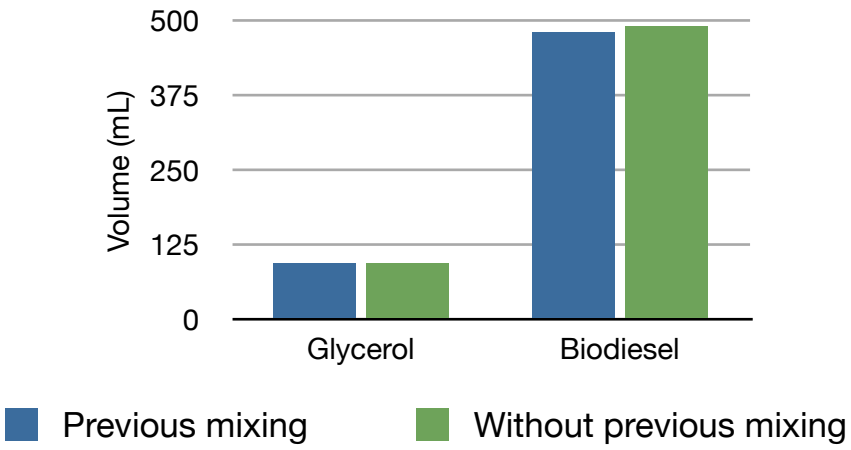


*Figure 6.3: Comparison of volumes with previous mixing of the methoxide and without it*

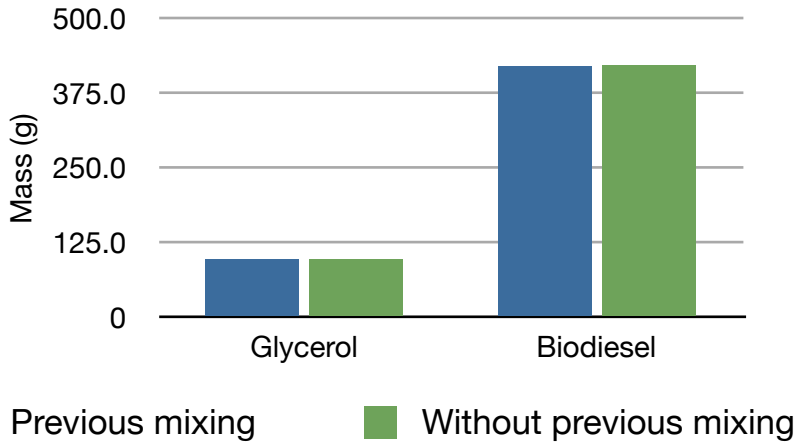


*Figure 6.4: Comparison of masses with previous mixing of the methoxide and without it*

As it can be seen in figures 6.3 and 6.4, both volumes and masses are almost equal when previous preparation of the methoxide was done and when it was not done. This means that the reaction could be done without preparing the methoxide previously, at least, when using potassium hydroxide as a catalyst. However, this was done with 500 mL of oil, it may imply more difficulties when doing it with big volumes because of the complications with the stirring.

#### 6.2.2.4 Adding the potassium hydroxide in two stages

This experiment was successful because the 3:27 test was passed when using both 6.2 and 6.8 grams of potassium hydroxide. It is important to note that when adding all the potassium methoxide at the same time and using 6.2 grams of potassium hydroxide, the 3:27 test was not passed. However, in this case, the test was passed, so catalyst could be saved using this method. On the other hand, the result of the solubility test when the catalyst was added in two stages was unsatisfactory, because it was much worse than the result obtained in other experiments.

Apart from that, this method implies more handling than when adding all the potassium methoxide at the same time, because there are two sedimentation stages instead of

one. Since the purpose of this thesis is to find an easy way to produce biodiesel, this option was dismissed. However, it could be used with satisfactory results and a lower catalyst consumption.

#### 6.2.2.5 Two stage acid-alkali reaction

Only one of the acid-alkali catalysed reactions was successful. This is probably because of the fact that only 50 mL of methanol was used in the second stage of the rapeseed reaction. Methanol, as explained previously, is essential for the reaction to be complete. The lack of methanol has two consequences, the first being an incomplete reaction and the second a low biodiesel yield. At the same time, when excess methanol is used, the glycerol volume obtained is higher than usual. Those phenomena are shown in figures 6.5 and 6.6, the first shows the volumes of methanol and the second the volumes of methanol. The data is about the products of the two acid-alkali catalysed reactions and of the potassium hydroxide catalysed reaction with standard conditions.

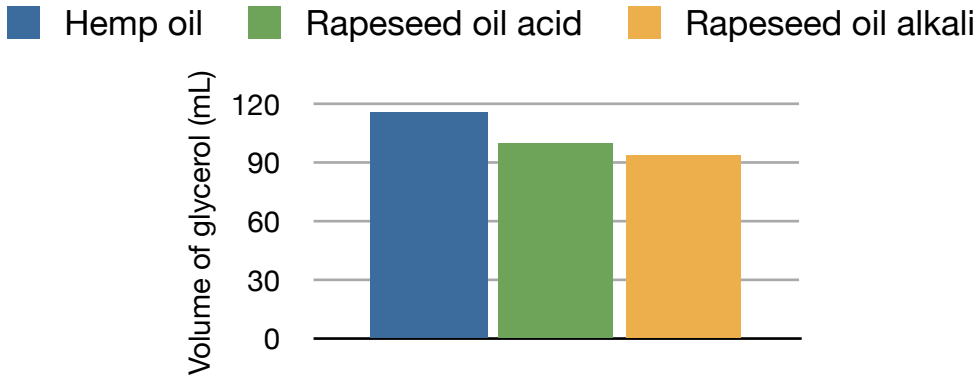


*Figure 6.5: Comparison of the volumes of glycerol obtained*

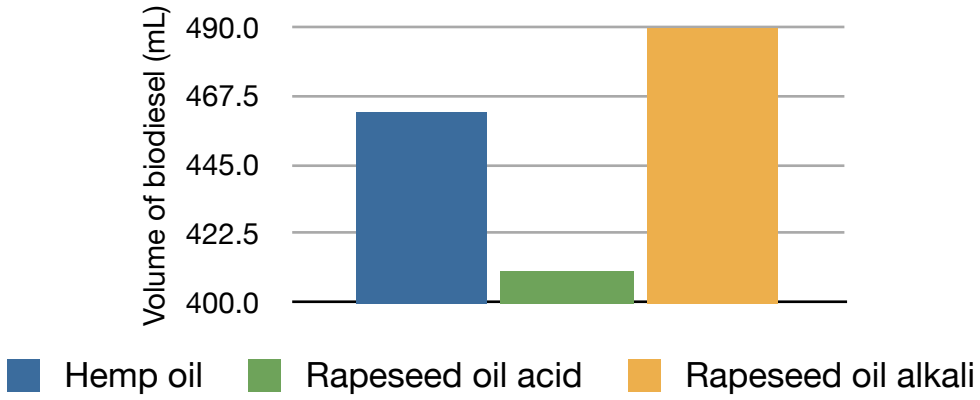


*Figure 6.6: Comparison of the volumes of biodiesel obtained*

### 6.2.3 Influence of methanol

The methanol experiments worked only when 20% methanol in volume was used for the reaction, when using lower volumes, the 3:27 test was not passed, that is, the reaction was incomplete. Nevertheless, not only was the reaction incomplete when

using low volumes of methanol, the glycerol obtained was also very viscous, making the sedimentation and separation steps complicated.

The reasons exposed above may indicate the necessity of using enough methanol on the reaction. However, methanol has several disadvantages when used in excess, because it stays in both biodiesel and glycerol phases of the products. Those products have to be cleaned of methanol, because it is a dangerous product that can pollute the soil, water, etc. Apart from that, biodiesel standards set maximum methanol amounts in its composition and methanol should also be removed before using dry cleaning products.

To sum up, a decision has to be taken with methanol. There are basically two options, the first of them is using excess methanol for the reaction, which will mean having a completely reacted biodiesel and having to remove the methanol from both biodiesel and glycerol phases. The other possible option is using lower methanol volumes, which will mean a not completely reacted product and more difficulties in the separation, but methanol will not have to be removed from the products. The first option appears to be more suitable when standardised biodiesel is wanted and the product is going to be sold, while the second is more appropriate when biodiesel for self consume is produced and it does not matter having unreacted oil in the biodiesel and not complying with the standards.

### 6.2.4 Influence of the temperature

The purpose of the different temperatures trials was to find out whether good results could be obtained at low temperatures and, also, find out the limits of the reaction. In fact, looking at the results, it could be determined that the reaction does not work when the temperatures are too low (3 ºC). It was explained in the results section that the stirring was not continuous in that case, but, since the experiment was repeated with the same stirring periods but at room temperature and the reaction was complete, it can be concluded that the stirring is not the determining factor. Indeed, the temperature is the controlling parameter.

There is another issue that should be carefully looked into when discussing the effects of the temperature. It is the production of glycerol (and the biodiesel production which is related to it), which varies highly with the temperature reaction. Figure 6.7 shows the different glycerol volumes which were obtained at different temperatures. The amount of methanol is higher when the reaction temperature is increasing. Moreover, the volume obtained at 60 ºC seems to be too high.

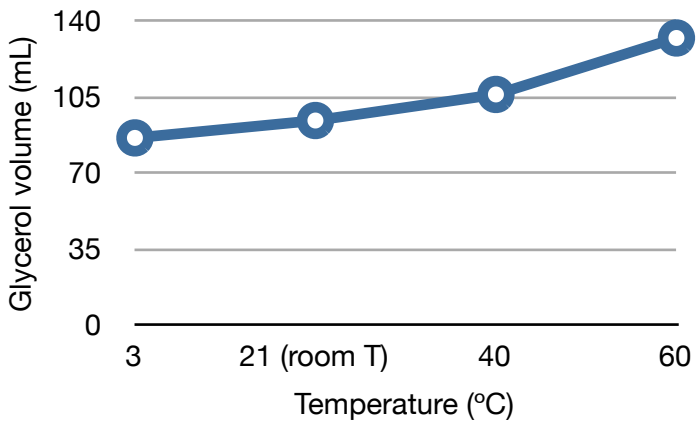


*Figure 6.7: Influence of the temperature on the glycerol volume*

One of the options that was considered to be a reason that could explain the high glycerol volumes was the reaction time. The reaction times found in the literature when temperatures around 60 ºC were used, was usually an hour or lower. In this case, however, the reaction time used was five hours. Therefore, the reaction was done at 60 ºC for one hour and a much lower volume of glycerol was obtained, as shown in figure 6.8.

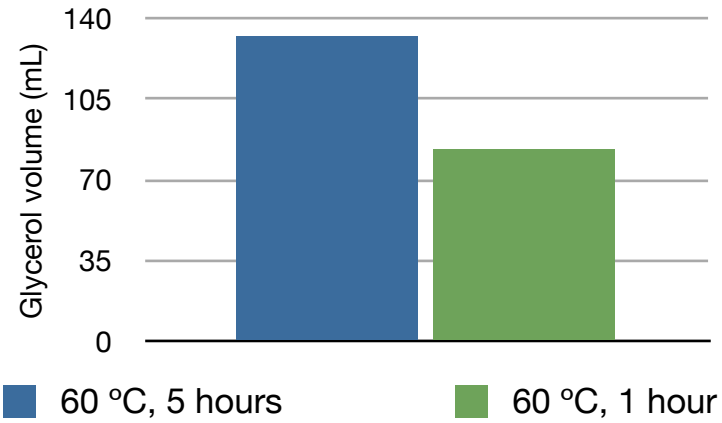


*Figure 6.8: Glycerol volumes after 1 hour and 5 hours reacting at 60 ºC*

Since the reaction was complete in both cases, the long reaction time seemed to be an explanation. However, there were another two issues that had to be explained yet, on the one hand, the glycerol obtained at 60 ºC is much more viscous than usual and the glycerol volume seemed to be too high to be just glycerol, some other compounds had to be there.

Explanation for both facts can be found. The glycerol was very viscous because of the evaporation of methanol, which, as explained previously, is necessary to obtain a less viscous glycerol. Methanol may have evaporated due to the high temperature. Besides, the mono and diglycerides seemed to dissolve in the glycerol phase, which would explain the very high glycerol volumes.

A trial with pure glycerol and raw biodiesel was done to determine the validity of this theory, the results are shown in table 6.1:

| Temperature (ºC) | $V_{biodiesel}$ (mL) | $V_{glycerol}$ (mL) | Reaction time (h) | $V_{glycerol}$ (mL) | $M_{glycerol}$ (g) | $V_{biodiesel}$ (mL) | $M_{biodiesel}$ (g) |
|---|---|---|---|---|---|---|---|
| 60 | 400 | 100 | 5 | 88 | 106.9 | 380 | 340.1 |

*Table 6.1: Biodiesel and pure glycerol results*

The volumes of both glycerol and biodiesel were lower after 5 hours, this may be partly explained by the evaporation of methanol, but there probably is also some dissolution of the mono and diglycerols from the biodiesel in the glycerol phase. In fact, glycerol, that at the beginning of the experiment had no colour, had certain yellow coloration when it finished.

### 6.2.5 Experiments with different kinds of oils

The fact that the transesterification reaction worked for four different kinds of oils at room temperature confirms the validity of the method. The variations in biodiesel and glycerol outputs can be explained because of the use of different methods (hemp oil was transesterified using the acid-alkali method, the other oils only used alkali catalyst) and because of the different properties of those oils. In figure 6.9, the biodiesel volumes obtained with different kinds of oils is displayed.

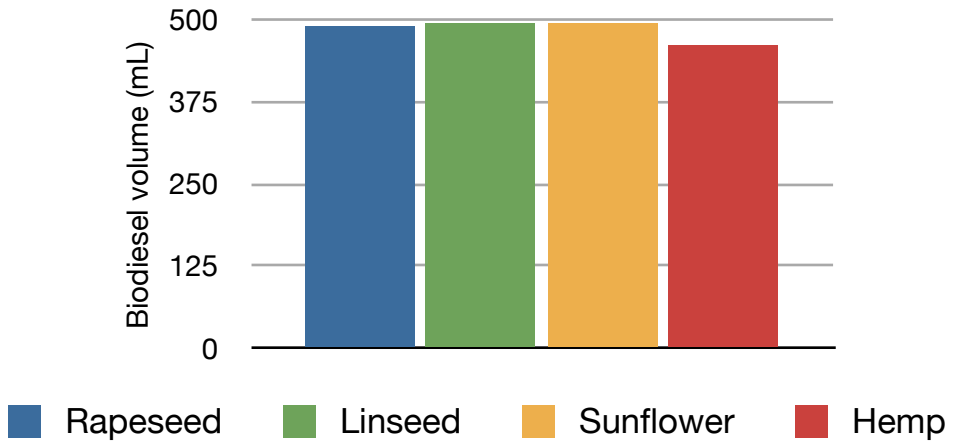


*Figure 6.9: Biodiesel production from different oil sources*

The lower volume obtained with hemp oil may be due to the fact that acid-alkali transesterification was used. In the other cases, the obtained biodiesel volume is almost the same.

## 6.3 Soap titration

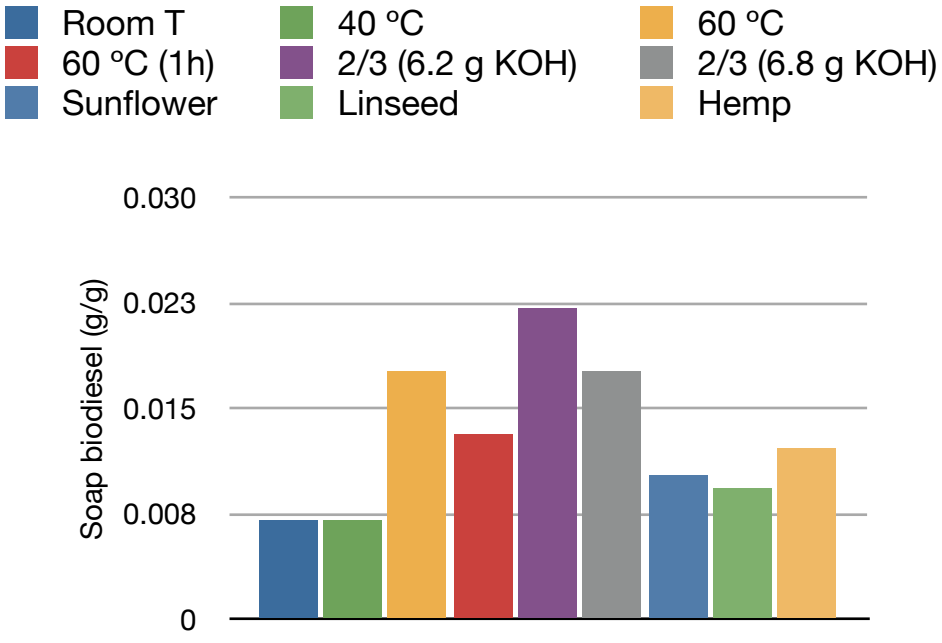


*Figure 6.10: Soap grams per gram of biodesel*

The amount of soap varies widely depending on how the biodiesel was done. Both experiments that were done using the 2/3 method, as well the experiments done at 60 ºC produce biodiesel with high soap amounts. This is consistent with the observations made in the solubility tests, which were much worse in those cases. The reason for the difference in the production of soaps is unknown. Finally, it should be noted that biodiesel produced at room temperature obtains the best result in the soap titration with biodiesel produced at 40 ºC.

## 6.4 Cleaning biodiesel

Four different dry products were tried, as well as water bubbling. The best results were obtained for water bubbling and Magnesol. However, the water bubbling cleaning took almost five days. Time is a powerful disadvantage of water bubbling when comparing it with other methods, because dry cleaning takes usually less than one hour, just 20 minutes for mixing and then some extra time for filtering the product. On the other hand, dry products are more expensive than water. Therefore, depending on different factors, the most suitable method will have to be decided for every manufacturers conditions.

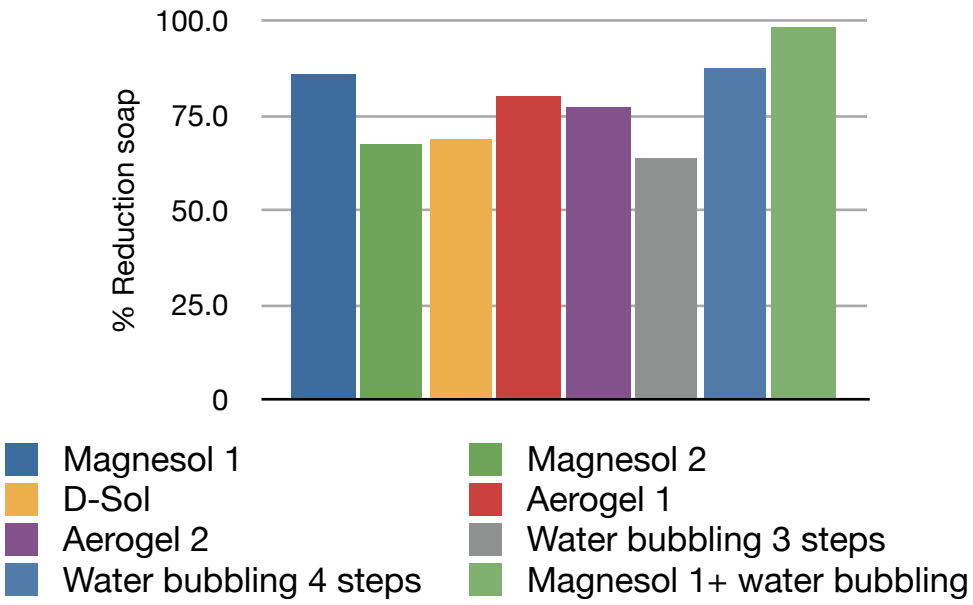


*Figure 6.11: Soap amount reduction with different products*

As mentioned, the best result is obtained for the combination of Magnesol and water bubbling, in that case 98% of the soap is removed. Water bubbling with four steps and Magnesol are also good options, but, in the case of Magnesol, two filtering papers were used, so this results are not significative.

## 6.5 Using the centrifuge

Five different trials were performed with the centrifuge and only one of them had a satisfactory result. It worked when using it to remove impurities from a raw sunflower oil. Consequently, its use is recommended when impurities from oils have to be removed, but different systems should be used to remove water from both biodiesel and oil and to separate glycerol and biodiesel, because it does not work with the centrifuge.

## 6.6 Methanol

During the making of the thesis, methanol has not been taken into account as a possible hazard in the products. This is an important issue, because several difficulties appear when methanol is present in any mixture. Biodiesel standards set a maximum methanol amount, the manufacturers of dry cleaning products recommend its removal before using their products and it has to be removed if glycerol has to be purified or if it is going to be used to produce soaps.

The reasons stated above show clearly how important the methanol removal is, but, methanol has a good property which facilitates this process, it is a very volatile product, so it will evaporate from biodiesel if left in contact with air. Methanol spilling on soils is a serious environmental risk, but its evaporation into air does not have any disadvantages.

When doing the experimental procedure for this paper, methanol was ignored, in fact, dry cleaning was done without removing it and it worked. Actually, there would probably not be too many inconveniences if using the biodiesel obtained without any methanol removal stages, but, it could always be left in contact with air for some time, just to make sure that no problems will appear.

A simple test was done with biodiesel that had been left in contact with air for some time (it was a mixture of different batches, so the time was different for each of them), the biodiesel was heated up to 120 ºC for two hours. It was weighed both before and after the heating and no significative reduction of weight was noticed, as shown in table 6.2.

| | $V_{biodiesel}$ (mL) | $W_{biodiesel}$ (g) |
|---|---|---|
| **Before heating** | 305 | 264.4 |
| **After heating** | 315 | 262.5 |

*Figure 6.2: Methanol removal*

To sum up, in this case methanol was not taken into account because it is not important for the purpose of the thesis, but, when producing biodiesel in big batches, its presence should be considered and a process to do so will probably be necessary.

# 7 CONCLUSION

First of all, it can be stated that the purpose of the thesis was fulfilled, a method for producing biodiesel at room temperature was developed and it seems to be valid, since complete transesterification of the oil is achieved. Moreover, the procedure has been tried with different oils and catalysts and worked in all cases.

Nevertheless, there are some limitations that may change the outcome if considered. Firstly, the fact that a detailed analysis of the biodiesel obtained could not be done because of the lack of a gas chromatography system. Because of this, simple analyses as the 3:27 test and soap titrations are the only proof of the validity of this method.

Another issue that deserves to be focused on is methanol. It has been disregarded during the experimental procedure because it is not a key question in this case, but it is when producing biodiesel in big quantities. Therefore, it should be considered when producing biodiesel that is going to be used by oneself or that is going to be sold.

As an extension to this thesis, another trial to produce biodiesel is going to be done. The difference between both studies is that in this new case, the volumes are going to be 1000 times larger. That is, instead of producing batches of biodiesel of 500 mL, batches of 500 litres are going to be obtained. In fact, this thesis is the pilot trial of the new system. It is right now being constructed in the same place where this thesis took place, the Faculty of Engineering and Sustainable Development, but it is not finished and it has not been tried yet. With this new development, it will be possible to find out whether biodiesel can also be produced without any heat in large batches, or if, on the contrary, that system only works in a lab scale. In the case that, as it is hoped, the large scale works, this method could be used by farmers to produce their own biodiesel, due to its simplicity and low cost. Using this system instead of a heated system means less expenditure on the equipment, because it is easier to find materials. It also implies less risks, since the use of heat is avoided. Moreover, to produce biodiesel in this way does not imply a big necessity to control the system, because nothing would happen if the reaction time is longer or if the raw biodiesel is left to stand for a while.

I believe that biodiesel may help to make our world more sustainable, but some conditions should be met. It is useless producing biodiesel in big factories, using oil that has been produced in another continent and then selling the biodiesel all over the world. Biodiesel is helpful when it is produced locally, using seeds that are adapted to the climate of the area, producing the oil next to the place where the crops are grown and, if possible, producing

the biodiesel in the same place, using a simple and cheap system. In this way, biodiesel will be a sustainable fuel and it may even help to developing countries.

Finally, this thesis is not complete if the issue of biodiesel versus food is not mentioned. I do believe that food is more important than fuels, as a matter of fact, human beings can live without cars but cannot live without eating. However, I think that the issue is not so simple. I understand that when producing the biodiesel in an industrial way, it is not sustainable and, many times, this can increase the price of different types of food. Nevertheless, since I believe in the production of biodiesel in a sustainable way and locally, I do not think that this would affect the prices of food. Mainly because farmers producing biodiesel would do so because they have soil available to grow these crops and, many times, the biodiesel will be for their own consumption. Besides, it should not be forgotten that biodiesel can be produced using waste vegetable oil, which does not compete with any kind of food to be attained. Therefore, I do understand the concerns of some people about biodiesel, but I think that, if produced in a sensible way, it can be helpful, but, of course, it will not be the solution to all our problems.

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# ANNEX I: PROPERTIES OF VEGETABLE OILS

| | Fatty acid composition (wt %) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Vegetable oil** | **12:0** | **14:0** | **14:1** | **16:0** | **16:1** | **18:0** | **20:0** | **20:1** | **22:0** | **24:0** | **18:1** | **22:1** | **18:2** | **18:3** | **18:4** | **6:0, 8:0, 10:0 and others** |
| Cottonseed | - | 0 | - | 28 | - | 1 | 0 | - | 0 | 0 | 13 | 0 | 58 | 0 | - | - |
| Tobacco | - | 0.09 | - | 10.96 | 0.2 | 3.34 | - | - | - | - | 14.54 | - | 69.49 | 0.69 | - | 0.69 |
| Rapeseed | - | 0 | - | 3 | - | 1 | 0 | - | 0 | 0 | 64 | 0 | 22 | 8 | - | - |
| Safflower | - | 0 | - | 9 | - | 2 | 0 | - | 0 | 0 | 12 | 0 | 78 | 0 | - | - |
| Sunflower | - | 0 | - | 6 | - | 3 | 0 | - | 0 | 0 | 17 | 0 | 74 | 0 | - | - |
| Sesame | - | 0 | - | 13 | - | 4 | 0 | - | 0 | 0 | 53 | 0 | 30 | 0 | - | - |
| Lindseed | - | 0 | - | 5 | - | 3 | 0 | - | 0 | 0 | 20 | 0 | 18 | 55 | - | - |
| Palm tree | - | | - | 35 | - | 7 | - | - | - | - | 44 | - | 14 | - | - | - |
| Corn | - | 0 | - | 12 | - | 2 | Tr | - | 0 | 0 | 25 | 0 | 6 | Tr | - | - |
| Tallow | - | - | - | 23.3 | 0.1 | 19.3 | - | - | - | - | 42.4 | - | 2.9 | 0.9 | 2.9 | - |
| Soya bean | - | - | - | 14 | - | 4 | - | - | - | - | 24 | - | 52 | - | 6 | - |
| Peanut | - | 0 | - | 11 | - | 2 | 1 | - | 2 | 1 | 48 | 0 | 32 | 1 | - | - |
| Coconut | 48.8 | 19.9 | - | 7.8 | 0.1 | 3.0 | - | - | - | | 4.4 | - | 0.8 | 0 | 65.7 | 8,9, 6,2 |
| Yellow grease | | 0.70 | 0.00 | 14.26 | 1.43 | 8.23 | 0.33 | 0.48 | - | - | 43.34 | - | 26.25 | 2.51 | 0.47 | - |

| Vegetable oil | Kinematic viscosity at 38ºC (mm2/s) | Cetane No. (ºC) | Heating Value (MJ/kg) | Cloud Point (ºC) | Pour Point (ºC) | Flash Point (ºC) | Density (kg/l) | Carbon residue (wt %) |
|---|---|---|---|---|---|---|---|---|
| Corn | 34.9 | 37.6 | 39.5 | -1.1 | -40 | 277 | 0.9095 | 0.24 |
| Cottonseed | 33.5 | 41.8 | 39.5 | 1.7 | -15 | 234 | 0.9148 | 0.24 |
| Crambe | 53.6 | 44.6 | 40.5 | 10.0 | -12.2 | 274 | 0.9048 | 0.23 |
| Linseed | 27.2 | 34.6 | 39.2 | 1.7 | -15.0 | 241 | 0.9236 | 0.22 |
| Peanut | 39.6 | 41.8 | 39.8 | 12.8 | -6.7 | 271 | 0.9026 | 0.24 |
| Rapeseed | 37.0 | 37.6 | 39.7 | -3.9 | -31.7 | 246 | 0.9115 | 0.30 |
| Safflower | 31.3 | 41.3 | 39.5 | 18.3 | -6.7 | 260 | 0.9144 | 0.25 |
| Sesame | 35.5 | 40.2 | 39.3 | -3.9 | -9.4 | 260 | 0.9133 | 0.24 |
| Soya bean | 32.6 | 37.9 | 39.6 | -3.9 | -12.2 | 254 | 0.9138 | 0.25 |
| Sunflower | 33.9 | 37.1 | 39.6 | 7.2 | -15.0 | 274 | 0.9161 | 0.27 |
| Palm | 39.6 | 42.0 | - | 31.0 | - | 267 | 0.9180 | 0.23 |
| Babassu | 30.3 | 38.0 | - | 20.0 | - | 150 | 0.9460 | - |
| Diesel | 3.06 | 50 | 43.8 | - | -16 | 76 | 0.855 | - |

Source: S.P. Singh, Dipti Singh, *Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review*, Renewable and Sustainable Energy Reviews 14 (2010), 200-216.

# ANNEX II: BIODIESEL STANDARDS

## 1.European Standard for Biodiesel: EN 14214

| Property | Testing method | Limits | | Unit |
|---|---|---|---|---|
| | | Min | Max | |
| Ester content | EN 14103 | 96.5 | | % (m/m) |
| Density at 15ºC | EN ISO 3675<br>EN ISO 12185 | 860 | 900 | kg/m$^3$ |
| Viscosity at 40ºC | EN ISO 3104, ISO 3105 | 3.5 | 5.0 | mm$^2$/s |
| Flash point | EN ISO 3679 | 120 | | ºC |
| Sulphur content | EN ISO 20846<br>EN ISO 20884 | | 10.0 | mg/kg |
| Carbon residue (on 10% distillation residue) | EN ISO 10370 | | 0.3 | % (m/m) |
| Cetane number | EN ISO 5165 | 51 | | |
| Sulphated ash content | ISO 3987 | | 0.02 | % (m/m) |
| Water content | EN ISO 12937 | | 500 | mg/kg |
| Total contamination | EN 12662 | | 24 | mg/kg |
| Copper strip corrosion (3h at 50º C) | EN ISO 2160 | 1 | | |
| Oxidation stability, 110ºC | EN 14112 | 6.0 | | h |
| Acid value | EN 14104 | | 0.5 | mg KOH/kg |
| Iodine value | EN 14111 | | 120 | g iodine/100g |
| Linolic acid methyl ester | EN 14103 | | 12 | % (m/m) |
| Fatty acid methyl esters (>=4 double bonds) | | | 1 | % (m/m) |
| Methanol content | EN 14110 | | 0.20 | % (m/m) |
| Monoglyceride content | EN 14105 | | 0.80 | % (m/m) |
| Diglyceride content | EN 14105 | | 0.20 | % (m/m) |
| Triglyceride content | EN 14105 | | 0.20 | % (m/m) |
| Free glycerol | EN 14105<br>EN 14106 | | 0.02 | % (m/m) |
| Total glycerol | EN 14105 | | 0.25 | % (m/m) |
| Alkaline metals (Na+K) | EN 14108, EN 14109 | | 5.0 | mg/kg |
| Alkaline earth metals (Ca+Mg) | prEN 14538 | | 5.0 | mg/kg |

| Property | Testing method | Limits | | Unit |
|---|---|---|---|---|
| | | Min | Max | |
| Phosphorus content | EN 14107 | | 10.0 | mg/kg |

*Source: BASF Group*

# 2.Specification for Biodiesel (B100) - ASTM D6751 - 08

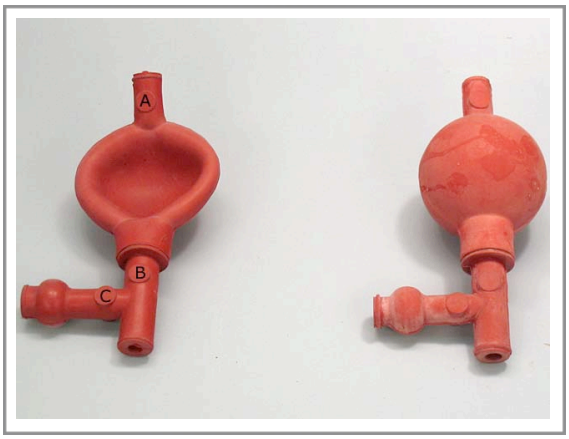
| Property | ASTM Method | Limits | Units |
|---|---|---|---|
| Calcium & Magnesium, combined | EN 14538 | 5 maximum | ppm (ug/g) |
| Flash Point (closed cup) | D 93 | 93 maximum | ºC |
| Alcohol Control (One of the following must be met) | | | |
| 1. Methanol Content | EN 14110 | 0.2 maximum | % volume |
| 2. Flash Point | D 93 | 130 minimum | ºC |
| Water & Sediment | D 2709 | 0.05 maximum | % volume |
| Kinematic Viscosity, 40 ºC | D 445 | 1.9-6.0 | mm2/s |
| Sulphated ash | D 874 | 0.02 maximum | % mass |
| Sulphur | | | |
| S 15 Grade | D 5453 | 0.0015 max. (15) | % mass (ppm) |
| S 100 Grade | D 5453 | 0.05 max. (500) | % mass (ppm) |
| Copper Strip Corrosion | D 130 | No. 3 maximum | |
| Cetane | D 613 | 47 minimum | |
| Cloud Point | D 2500 | report | ºC |
| Carbon Residue 100% sample | D 4530 | 0.05 maximum | % mass |
| Acid Number | D 664 | 0.50 maximum | mg KOH/g |
| Free Glycerin | D 6584 | 0.020 maximum | % mass |
| Total Glycerin | D 6584 | 0.240 maximum | % mass |
| Phosphorus Content | D 4951 | 0.001 maximum | % mass |
| Distillation, T90AET | D 1160 | 360 maximum | ºC |
| Sodium/Potassium, combined | EN 14538 | 5 maximum | ppm |
| Oxidation Stability | EN 14112 | 3 minimum | hours |
| Cold Soak Filtration | Annex to D6751 | 360 maximum | seconds |
| For use in temperatures below -12 ºC | Annex to D6751 | 200 maximum | seconds |

*Source: the National Biodiesel Board*

# ANNEX III: LABORATORY EQUIPMENT

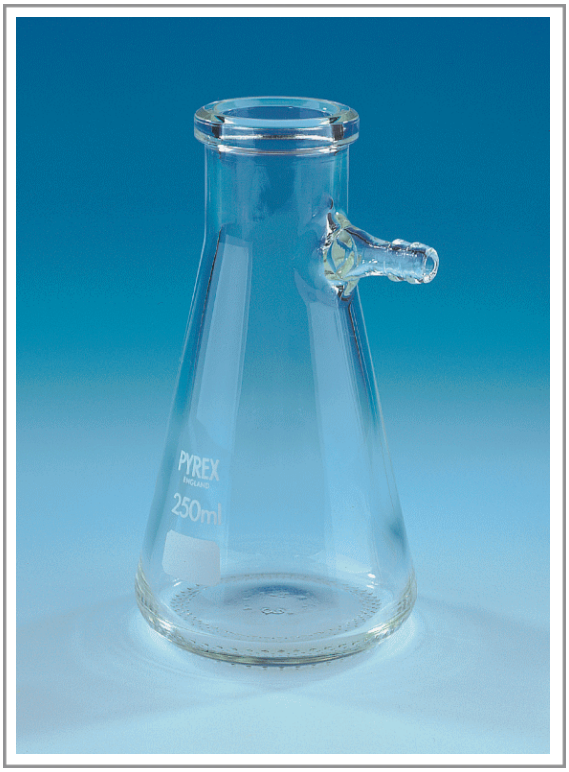
In the table the pictures and names of all the laboratory equipment which was used during the project can be seen:

| | |
|---|---|
| | |
| **Erlenmeyer [1]** | **Beaker [2]** |
| | |
| **Weight balance [3]** | **Magnetic stirrer [4]** |

| | |
|---|---|
|  | |
| **Pipette bulb [5]** | **Pipette [6]** |
| | |
| **Burette [7]** | **Separatory funnel [8]** |

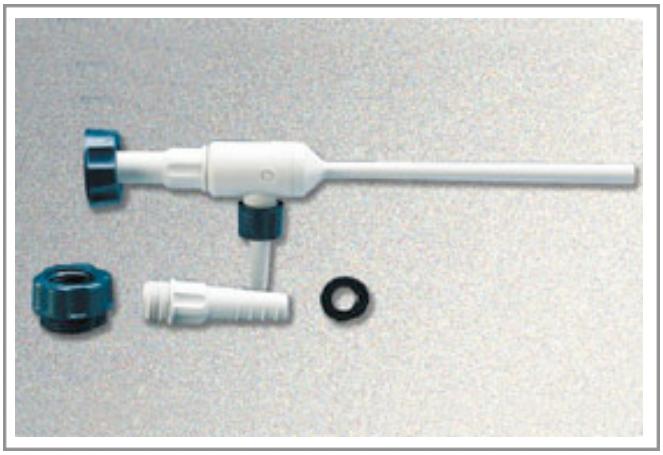
Graduated cylinder [9]

Volumetric flask [10]




Kitasato flask [11]

Büchner funnel [12]

| |  |
|---|---|
| **Filter paper [13]** | **Vacuum pump [14]** |

Sources:

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[12] Buchner funnel, http://commons.wikimedia.org/wiki/File:Buchner_funnel.jpg, Access 2010-06-26.

[13] Hangzhou Special Paper Industry Co., Ltd., http://special-paper.en.made-in-china.com/product/hbeEpIGVgJkO/China-Chemical-Analysis-Filter-Paper.html, Access 2010-06-26.

[14] Labolan, *Water Jet Vacuum Pump*, http://www.labolan.es/detalles-producto.php?idarea=18&p=1547&lang=en, Access 2010-06-26.

# ANNEX IV: AIR FLOW MACHINE

For the production of air bubbles in the water cleaning part an air flow machine is needed. For this thesis a ‘SuperFish AirFlow 4’ was used, its main characteristics are:

- 4 outputs to connect to airstones, filters etc.
- Air flow rate of 10 L/min
- Adjustable air flow
- Low power usage of 10 watts
- Low noise

# ANNEX V: DRY CLEANING PRODUCTS

## 1.Magnesol

Magnesol is a synthetic magnesium silicate adsorbent, which is used as an adsorbent filter aid. It ensures biodiesel quality by removed contaminants that can be found within the methyl esters. It is manufactured by The Dallas Group of America. It is composed by magnesium silicate in a 97%. Different articles and the material safety data sheet for Magnesol can be found in the next pages.

## 2.D-Sol

As well as Magnesol, D-Sol is manufactured by The Dallas Group of America, it is used in the same way as Magnesol, the main difference between them is their composition. Magnesol is composed by magnesium silicate (97% minimum), while D-Sol is composed in a 70% by magnesium silicate and the rest 30% is a component B, which is secret. In the next pages, the material safety data for D-Sol and more information about it can be found.

## 3.Aerogel

Svenska Aerogel AB has developed an aerogel-like silicate material which has the potential to be used as a generic adsorbent. The route for making the aerogel-like adsorbent involves the precipitation of silica using alkali silicates and certain bi- and trivalent metal ions. In many respects, the precipitated silica material shows great similarities with the classic silica aerogel invented already in the 1930's but involves a less complicated route of processing, higher flexibility and the use of cheaper feedstock chemicals.

Depending on the application the material can be made as a filler material with a typical size range of 5 – 75µm or as coarser aggregates or granules having a characteristic size of up to 10mm. The specific surface area (BET-area) is typically 400m2/g. The bulk density of granules as well as filler is typically less than 0.40kg/m3.

The substrate material is environmentally friendly and consists solely of benign chemicals and common elements such as Si, Ca and Mg.

Two different materials were used in the biodiesel trials, one of them is a spray dried magnesium silicate material which has a particle range of 5-75 micrometers. The other material is a calcium magnesium (35/65) silicate impregnated with 8% potassium hydroxide and a particle range smaller than 250 micrometers.

The Dallas Group of America, Inc.
374 Route 22 • P.O. Box 489, Whitehouse, NJ 08888
1.908.534.7800 • 1.908.534.0084 (fax)
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# MATERIAL SAFETY DATA SHEET
## (Conforms to US CFR 1910.1200 and REACH EC 1907/2006)

**Date of Issue: March 9, 2009**

## 1 IDENTIFICATION OF SUBSTANCE

1.1 PRODUCT NAME: MAGNESIUM SILICATE, synthetic, amorphous, hydrous

TRADE NAME: D-SOL®

GRADES: D Series

1.2 Use of the substance: Adsorbent, filter aid, flow agent

1.3 Supplier: The Dallas Group of America, Inc.
374 Route 22
P.O. Box 489
Whitehouse, NJ 08888 Tel: 908-534-7800 FAX: 908-534-0084
Information department: Product Safety Department

1.4 Emergency Telephone: Not required for non-hazardous substances.

## 2 HAZARDS IDENTIFICATION

Magnesium silicate is not explosive, flammable, or combustible. It is a mild irritant to eyes, skin, and respiratory passages (see Section 11)

Not classified as dangerous under EU Directive 67/548/EEC

HMIS ratings (scale 0-4)

Health = 0
Fire = 0
Reactivity = 0

## 3 COMPOSITION/DATA ON INGREDIENTS

| CAS No. | EINECS No. | Description | % |
|---|---|---|---|
| 1343-88-0 | 215-681-1 | Magnesium Silicate | 97 - 100 |

## 4 FIRST AID MEASURES

| | |
|---|---|
| Inhalation: | Drink water to clear the throat, blow nose to clear respiratory passages. |
| Ingestion: | Incidental ingestion of this product does not require first aid. |
| Skin Contact: | Wash exposed area thoroughly with soap and water. |
| Eye Contact: | Flush eyes with plenty of water. Call a physician if irritation persists. |

## 5 FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA: Select the proper media to extinguish a surrounding fire.
No special protective equipment for firefighters is required.

## 6 ACCIDENTAL RELEASE MEASURES

| | |
|---|---|
| SPILL CLEANUP METHODS: | Sweep or vacuum spilled material. The use of a sweeping compound/dust suppressant is suggested.<br>Make sure that all personnel involved in housekeeping and spill clean up follow good industrial hygiene practices and wear proper personal protective equipment. |

## 7 HANDLING AND STORAGE

| | |
|---|---|
| USAGE PRECAUTIONS: | None in designated use. |
| STORAGE PRECAUTIONS: | None in designated use. |
| STORAGE CRITERIA: | No special requirements. |

## 8 EXPOSURE CONTROLS AND PERSONAL PROTECTION

8.1 Exposure Limit Values: The American Conference of Government Industrial Hygienists (ACGIH) does not list synthetic magnesium silicate in the substance index. A threshold limit value - time weighted average (TLV-TWA) of 10 $mg/m^3$ of total dust is recommended for substances for which no specific TLVs have been assigned.

In the European Union, comply with all EU, Member State, and local guidelines.

8.2 Exposure Controls: No special requirements

8.3 Occupational Exposure Controls:

PROTECTIVE EQUIPMENT

| | |
|---|---|
| VENTILATION: | No special requirements. |
| RESPIRATORS: | If the airborne concentration exceeds the ACGIH recommended TLV, an approved dust mask should be worn. |
| PROTECTIVE GLOVES: | Not required. |
| EYE PROTECTION: | Not required. |
| OTHER PROTECTION: | Not required. |
| HYGIENIC WORK ROUTINES: | No special requirements. |

## 9 PHYSICAL AND CHEMICAL PROPERTIES

| | |
|---|---|
| Normal Physical State @ 20°C (68°F): | White, odorless powder |
| pH (1 in 10 slurry) | 7.0 to 10.8 |
| Melting Point: | 1910°C (3470°F) |
| Absolute Density ($H_20$ = 1) | 2.10 - 2.20 |
| Solubility in Water: | Magnesium Silicate is insoluble |
| Vapor Pressure: | N/A* |
| Viscosity: | N/A* |
| Boiling Point: | N/A* |
| Vapor Density: | N/A* |
| % Volatile: | N/A* |
| Evaporation Rate: | N/A* |
| Ignition Temperature: | N/A* |

*N/A - Not applicable

## 10 STABILITY AND REACTIVITY

| | |
|---|---|
| 10.1 Conditions to avoid | None in designated use |
| 10.2 Materials to avoid | None in designated use |
| 10.3 Hazardous Decomposition Products | None, the substance is stable |

**Note:** In sufficient quantity, a filter cake composed of a flammable organic liquid absorbed on synthetic magnesium silicate or other filter materials such as diatomaceous earth, Perlite, or natural clays may be self-heating or possibly pyrophoric.

- A self-heating material is a material that, when in contact with air and without an energy supply, is liable to self-heat. A material of this type which exhibits spontaneous ignition or if the temperature of the sample exceeds 200 °C (392 °F) during the 24-hour test period when tested in accordance with UN Manual of Tests and Criteria, is classed as a Division 4.2 material.
- A pyrophoric material is a liquid or solid that, even in small quantities and without an external ignition source, can ignite within five (5) minutes after coming in contact with air when tested according to the UN Manual of Tests and Criteria.

## 11 TOXICOLOGICAL INFORMATION

This product does not contain any ingredient designated by IARC, NTP, ACGIH, or OSHA as probable or suspected human carcinogens.

Studies conducted in 1989 at Hill Top Biolabs, Inc., Cincinnati OH evaluated MAGNESOL® products with the formula $MgO{:}2.6SiO_2$ for acute oral toxicity (albino male rat), acute dermal toxicity (albino rabbit), skin irritation (albino rabbit) and eye irritation (albino rabbit) according to the techniques specified in the U.S. Federal Hazardous Substances Act. The conclusions of those studies were:

a. MAGNESOL® is classified as non-toxic by oral administration.
b. It is not a primary skin irritant or a corrosive by dermal application.
c. It is not classified as toxic by dermal administration.
d. It is classified in Toxicity Category III (corneal involvement or irritation clearing in 7 days or less) by ocular administration.

## 12 ECOLOGICAL INFORMATION

WATER HAZARD CLASSIFICATION: Not a known pollutant.

This Substance does not meet PBT or vPvB criteria under Annex XIII of REACH

## 13 DISPOSAL CONSIDERATIONS

DISPOSAL METHODS: In the form supplied, magnesium silicate is not classified as a hazardous waste in the U.S. or the EU. Magnesium silicate may undergo normal non-hazardous waste disposal.

However, under RCRA, it is the responsibility of the user of products to determine, at the time of disposal, whether the product falls under RCRA as a regulatory waste. The product uses, transformations, synthesis, mixtures, etc., may render the resulting end product subject to regulation. See Section 10 for additional information on filter cakes.

## 14 TRANSPORT INFORMATION

| | |
|---|---|
| DOT CLASS: | Not Regulated |
| UN/NA NO.: | Not Classified |
| FREIGHT CLASSIFICATION: | NMFC - 48210 Column 55 |
| IMO CLASS: | Not Classified |
| ADR/RID: | Not Classified |

Comply with all EU, national, and local regulations.

## 15 REGULATORY INFORMATION

This substance is not classified as dangerous according to EU Directive 67/548/EEC.
This material is not listed in Sections 302, 312, or 313 of US SARA III.
It is reported in the US TSCA Inventory, 1986.
This substance has been pre-registered under REACH.
A Chemical Safety Assessment has not yet been carried out for this substance.

## 16 OTHER INFORMATION

| | |
|---|---|
| Approximate chemical formula: | $MgO:2.6SiO_2$ |
| International Numbering System (INS) number: | 553i |
| European Union E number: | E553a(i) |
| EINECS number: | 215-681-1 |

References A through D are specific to synthetic magnesium silicate with the approximate chemical formula $MgO:2.6SiO_2$:

A. 21 CFR Part 182, Subpart C - Generally recognized as safe.
B. Clinical Toxicology of Commercial Products, Edition 4, 1976 - No acute toxicology recognized.
C. NIOSH Registry of Toxic Effects of Chemical Substances, Vol. 2, 1986 - Irritation data: Human skin - 300 micro gram/3 days. Very mild.
D. Magnesium silicate with an approximate chemical formula of $MgO:2.6SiO_2$ is not listed in:
    1. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man, 1988
    2. Industrial Hygiene and Toxicology, F. A. Patty
    3. Industrial Toxicology, Alice Hamilton and Harriet Hardy
    4. Toxicology of the Eye, W. Morton Grant
    5. Dangerous Properties of Industrial Materials, Sax and Lewis
    6. Government Publications:
        a. NIOSH/OSHA Pocket Guide to Chemical Hazards
        b. Registry of Toxic Effects of Chemical Substances
        c. The Industrial Environment - It's Evaluation and Control
    7. Annex I to Directive 67/548/EEC

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The data contained herein is being supplied for the limited purpose of complying with the OSHA "Right-to-Know" Regulation, 29 CFR 1910.1200. The submission of this MSDS may be required by law but this is not an assertion that this substance is hazardous when used in accordance with proper safety practices and normal handling procedures.

FOR MORE INFORMATION CALL 812-283-6675 Revised 08-2-09

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374 Route 22 • P.O. Box 489, Whitehouse, NJ 08888
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www.dallasgrp.com

# MATERIAL SAFETY DATA SHEET
## (Conforms to CFR 1910.1200)

## 1 IDENTIFICATION OF SUBSTANCE

PRODUCT NAME: *D-SOL®*

GRADES: 300R

SUPPLIER: The Dallas Group of America, Inc.
374 Route 22
P.O. Box 489
Whitehouse, NJ 08888 Tel: 908-534-7800 FAX: 908-534-0084

Information department: Product Safety Department

## 2 COMPOSITION/DATA ON INGREDIENTS

| Component | CAS No. | Approximate % |
|---|---|---|
| Magnesium Silicate | 1343-88-0 | 70 |
| Component B * | | 30 |

* The identity of Component B is being withheld as a trade secret per 29CFR 1201.12(i).

## 3 HAZARDS IDENTIFICATION

*D-SOL®* 300R has not been evaluated as a single product. The information in this section pertains mainly to Component B as Magnesium Silicate is not explosive, flammable, or combustible and is only a mild irritant to eyes, skin, and respiratory passages.

Inhalation: Causes irritation to mucous membranes and respiratory passages.

Ingestion: Causes irritation to the mouth and digestive tract.

Skin Contact: Causes irritation.

Eye Contact: Corrosive, causes burns.

**HMIS ratings (scale 0-4)**

**Magnesium silicate**

Health = 0
Fire = 0
Reactivity = 0

**Component B**

Health = 1
Fire = 0
Reactivity = 0

## 4 FIRST AID MEASURES

*D-SOL*® 300R has not been evaluated as a single product. The information in this section pertains mainly to Component B alone as Component A is only a mild irritant to eyes, skin, and respiratory passages.

| | |
|---|---|
| Inhalation: | Remove to fresh air. |
| Ingestion: | If swallowed, DO NOT INDUCE VOMITING. Give large glasses of water. If vomiting occurs spontaneously, keep airway clear and give more water. |
| Skin Contact: | Flush thoroughly with cool water under shower. Wash contaminated clothing and thoroughly clean shoes before reuse. |
| Eye Contact: | Immediately flush eyes with a directed stream of water for at least 15 minutes. Remove contact lenses if worn. Washing eyes within several seconds essential to achieve maximum effectiveness. |
| **For all of the above:** | **GET MEDICAL ATTENTION IMMEDIATELY** |

## 5 FIRE FIGHTING MEASURES

| | |
|---|---|
| EXTINGUISHING MEDIA: | D-SOL® 300-R is not explosive, flammable, or combustible. Select the proper media to extinguish a surrounding fire. |

## 6 ACCIDENTAL RELEASE MEASURES

| | |
|---|---|
| SPILL CLEANUP METHODS: | Dry material can be swept or shoveled up. Avoid generating dust. Flush residue with water. Observe environmental regulations.<br><br>Make sure that all personnel involved in housekeeping and spill clean-up follow good industrial hygiene practices and wear proper personal protective equipment. |

## 7 HANDLING AND STORAGE

| | |
|---|---|
| USAGE PRECAUTIONS: | None in designated use. |
| STORAGE PRECAUTIONS: | None in designated use. |
| STORAGE CRITERIA: | Do not store in aluminum container or use aluminum fittings or transfer lines as flammable hydrogen gas can be generated. |

## 8 EXPOSURE CONTROLS AND PERSONAL PROTECTION

| | |
|---|---|
| VENTILATION: | No special requirements. |
| RESPIRATORS: | Wear a NIOSH/MSHA approved dust mask where airborne contaminants occur. |
| PROTECTIVE GLOVES: | Wear chemical resistant gloves such as rubber, neoprene, or vinyl. |
| EYE PROTECTION: | Chemical goggles. |
| OTHER PROTECTION: | Full cover clothing. |
| HYGIENIC WORK ROUTINES: | Emergency shower and eyewash facility should be in close proximity |

## 9 PHYSICAL AND CHEMICAL PROPERTIES

| | Magnesium silicate | Component B |
|---|---|---|
| Physical State @ 68°F | White powder | White powder |
| Melting Point: | 3470° F | |
| Absolute Density ($H_20$ = 1): | 2.10 - 2.20 | |
| Solubility in Water: | insoluble | complete |
| Vapor Pressure: | N/A* | N/A* |
| Viscosity: | N/A* | N/A* |
| Boiling Point: | N/A* | N/A* |
| Vapor Density: | N/A* | N/A* |
| % Volatile: | N/A* | N/A* |
| Evaporation Rate: | N/A* | N/A* |
| Ignition Temperature: | N/A* | N/A* |

*N/A - Not applicable

## 10 STABILITY AND REACTIVITY

| | |
|---|---|
| Stability: | Stable |
| Polymerization: | Will not and cannot occur |
| Conditions and Materials to Avoid | None in designated use. |

**Note:** In sufficient quantity, a filter cake composed of a flammable organic liquid absorbed on synthetic magnesium silicate or other filter materials such as diatomaceous earth, Perlite, or natural clays may be self-heating or possibly pyrophoric.

- A self-heating material is a material that, when in contact with air and without an energy supply, is liable to self-heat. A material of this type which exhibits spontaneous ignition or if the temperature of the sample exceeds 200 °C (392 °F) during the 24-hour test period when tested in accordance with UN Manual of Tests and Criteria, is classed as a Division 4.2 material.
- A pyrophoric material is a liquid or solid that, even in small quantities and without an external ignition source, can ignite within five (5) minutes after coming in contact with air when tested according to the UN Manual of Tests and Criteria.

## 11 TOXICOLOGICAL INFORMATION

Magnesium silicate:

| | | |
|---|---|---|
| A. | Albino male rat: | Acute oral - LD50 > 5.0 g/kg |
| B. | Albino rabbit: | Acute dermal - LD50 > 2.0 g/kg<br>Primary Irritation Index 0.80<br>0 = No erythema (skin redness)<br>1 = Very slight erythema |
| C. | Albino rabbit: | Eyes – Toxicity category III; irritation clearing in 7 days or less. |

The above study was performed by Hill Top Biolabs, Inc. Cincinnati, OH, in 1989 and was specific to magnesium silicate with the formula $MgO:2.6SiO_2$. The conclusions of this test were:

a. Magnesium silicate is classified as non-toxic by oral administration.
b. It is not a primary skin irritant or a corrosive by dermal application.
c. It is not classified as toxic by dermal administration.
d. It is classified in Toxicity Category III by ocular administration.

## 11 TOXICOLOGICAL INFORMATION, continued

Component B:

OSHA Permissible Exposure Limit (PEL) and ACGIH Threshold Limit Value (TLV) have not been established. The recommended ceiling limit is 2 $mg/m^3$ respirable dust.

This product does not contain any ingredient designated by IARC, NTP, ACGIH, or OSHA as probable or suspected human carcinogens.

## 12 ECOLOGICAL INFORMATION

*D-SOL*® 300R is inorganic and not subject to biodegradation. There is no data available on the environmental fate of this material.

Magnesium silicate is not a known pollutant.

Component B is not a listed toxic chemical under SARA III, §302, §304, or §313. The high pH (alkalinity) of the undiluted or unneutralized material is harmful to aquatic life.

## 13 DISPOSAL CONSIDERATIONS

DISPOSAL METHODS: The components of *D-SOL*® 300R are not regulated under RCRA landfill requirements. However, unneutralized material is a RCRA Hazardous Waste because it exhibits the corrosive characteristic as defined in EPA rules at 40 CFR §261.22 (a)(1). Under RCRA, it is the responsibility of the user of products to determine, at the time of disposal, whether the product falls under RCRA as a regulatory waste. See Section 10 for additional information on filter cakes.

## 14 TRANSPORT INFORMATION

| | |
|---|---|
| DOT CLASS: | Not applicable. |
| DOT Hazardous Substance: | Not applicable. |
| DOT Marine Pollutant: | Not applicable. |
| UN/NA NO.: | Not Classified |
| FREIGHT CLASSIFICATION: | NMFC - 48210 Column 55 |
| IMO CLASS: | Not Classified |

## 15 REGULATORY INFORMATION

The components of D-SOL® 300R are reported in the TOSCA Inventory, 1986.
The components of D-SOL® 300R are not listed in Sections 302, 312, or 313 of SARA III.

## 16 OTHER INFORMATION

| | | |
|---|---|---|
| APPROXIMATE CHEMICAL FORMULA: | Magnesium silicate | $MgO:2.6SiO_2$ |
| | Component B | Trade secret |

References A through C and E are specific to magnesium silicate with the approximate chemical formula $MgO:2.6SiO_2$:

A. 21 CFR Part 182, Subpart C - Generally recognized as safe.
B. Chemical Toxicology of Commercial Products, Edition 4, 1976 - No acute toxicology recognized.
C. NIOSH Registry of Toxic Effects of Chemical Substances, Vol. 2, 1986 - Irritation data: Human skin-300 micro gram/3 days. Very mild.
D. American Conference of Government Industrial Hygienists - The ACGIH does not list magnesium silicate in the substance index. A threshold limit value - time weighted average (TLV-TWA) of 10 $mg/m^3$ of total dust is recommended for substances for which no specific TLVs have been assigned.
E. Magnesium silicate with an approximate chemical formula of $MgO:2.6SiO_2$ is not listed in:
    1. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man, 1988
    2. Industrial Hygiene and Toxicology, F. A. Patty
    3. Industrial Toxicology, Alice Hamilton and Harriet Hardy
    4. Toxicology of the Eye, W. Morton Grant
    5. Dangerous Properties of Industrial Materials, Sax and Lewis
    6. Government Publications:
        a. NIOSH/OSHA Pocket Guide to Chemical Hazards
        b. Registry of Toxic Effects of Chemical Substances
        c. The Industrial Environment - It's Evaluation and Control

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FOR MORE INFORMATION CALL 812-283-6675 Revised 10-27-2009

# D-SOL®

## Quality Comparison Summary

- **SAVES TIME...** Purify biodiesel in minutes, not hours and with no messy emulsions.
- **SAVES ENERGY...** No drying required.
- **SAVES CAPITAL...** No expensive centrifuges, dryers, and no large settling tanks.
- **DRY WASH™...** D-SOL adsorbent technology requires no wash water and produces no waste water.

*Magnesol D-SOL is the first in Dry Wash™ technology...*
*For more information, contact us today!*

| SPECIFICATIONS | | | RAPESEED METHYL ESTERS | | | SOYBEAN METHYL ESTERS | | | YELLOW GREASE METHYL ESTERS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | ASTM D6751 | EN 14214 | Initial Sample | Washed & Dried | 0.5% D-SOL D60 | Initial Sample | Washed & Dried | 0.5% D-SOL D60 | Initial Sample | Washed And Dried | 1.5% D-SOL D60 |
| Soap, mg/kg | None | None | 637 | 30 | 0 | 651 | 13 | 0 | 1900 | 91 | 0 |
| Free Glycerin, % | 0.020 max | 0.020 max | 0.053 | 0.000 | 0.005 | 0.033 | 0.002 | 0.000 | 0.063 | 0.037 | 0.002 |
| Total Glycerin, % | 0.240 max | 0.250 max | 0.217 | 0.162 | 0.162 | 0.209 | 0.196 | 0.186 | 0.220 | 0.185 | 0.143 |
| Flash Point, °C | 130 min | 120 min | 90 | 130 | 140 | 80 | 143 | 150 | 100 | 158 | 155 |
| Metals I Na+K, mg/kg | 5.0 max | 5.0 max | 53 | 3 | 0 | 61 | 5 | 0 | 67 | 3 | 0 |
| Metals II Mg+Ca, mg/kg | 5.0 max | 5.0 max | 6 | 5 | 0 | 4 | 0 | 0 | 8 | 0 | 0 |
| Oxidation Stability @ 110°C, hours | 3.0 min | 6.0 min | 0.61 | 0.65 | 2.25 | 0.5 | 0.6 | 3.7 | 0.5 | 0.6 | 4.3 |
| Water, mg/kg | 500 max | 500 max | 400 | 350 | 378 | 1000 | 150 | 300 | 7000 | 600 | 50 |
| Sulfated Ash, mass % | 0.020 max | 0.020 max | 0.056 | 0.002 | 0.000 | 0.060 | 0.005 | 0.000 | 0.08 | 0.010 | 0.002 |
| Methanol Content, % | None | 0.2 max | 0.19 | 0.015 | 0.009 | 0.15 | 0.001 | 0.011 | 0.116 | 0.001 | 0.002 |

**PHONE** [1] 812-283-6675 Ext. 5 **EMAIL** biodiesel@dallasgrp.com **WEB** www.dallasgrp.com

DALLAS SPECIALTY ADSORBENTS

0705I205

# Adsorbing It All

**With a solid track record in oleo-chemical purification, The Dallas Group has entered the biodiesel industry with a synthetic magnesium silicate adsorbent that has changed the way some producers clean up their methyl esters.**

By Tom Bryan

The Dallas Group of America Inc., a recognized leader in oleo-chemical purification technology, is arguably the only U.S. company actively marketing a commercial product for the adsorptive purification of biodiesel. The company's synthetic magnesium silicate adsorbent, sold under the trademarked name Magnesol, is an "adsorbent filter aid" that ensures biodiesel quality by removing contaminants within methyl esters. Subsequently, the removal of contaminants enables biodiesel producers to guarantee that the fuel they produce meets ASTM D-6751 specifications and other industry standards.

The Dallas Group broke into the North American biodiesel market with Magnesol only recently, but according to one producer, the adsorbent could be "a cure-all for most process upsets and impurity problems" that occur during biodiesel production. Multiple customers nationwide in the edible oils industry are already using the product. Bryan Bertram, director of industrial sales with The Dallas Group, believes the U.S. biodiesel market represents one of the next big opportunities for the product line. In an interview with *Biodiesel Magazine*, Bertram, along with Chris Abrams, business development manager, and Brian Cooke, product development specialist, discussed the company's ongoing efforts with Magnesol. Bertram said the product increases the oxidative stability of biodiesel and is used in conjunction with—or in place of—the water-wash treatment in the biodiesel production process.

After the glycerin separation process, methyl esters contain contaminant materials that are detrimental to the quality of the fuel and must be eliminated from the product. Reduction of the water-soluble contaminants, traditionally, is accomplished by water-washing the biodiesel. However, according to Bertram, the era of the biodiesel water-wash may be gradually ending. "The water-wash method does nothing to remove the water-insoluble impurities," he told *Biodiesel Magazine*. "And due to the resulting effluent water, it gives cause for environmental concerns."

With Magnesol, the water-wash step can be eliminated, and so can the liquid separation and drying of biodiesel. "It can also replace other methods of removing chlorophyll, metals, and color from biodiesel," Bertram said. "If the processor is utilizing a costly distillation step on the tail end to remove metals or other contaminants, they could forgo that step also. In addition, Magnesol has a high affinity for methanol and water, so it will remove the last bits from methl esters.."

**What is perhaps most attractive about Magnesol, is that it works simply and relatively inexpensively.**

Purification with Magnesol also increases the oxidative stability of biodiesel, Bertram said, which is becoming increasingly important, due to the demands being placed on fuel producers by the auto manufacturing industry and government.

Magnesol, which can be used in either

batch or continuous processes, removes residual methanol, providing a cost savings in the stripping step. Magnesol is able to remove sulfur, which is especially important in light of impending U.S. EPA regulations that will limit sulfur in diesel fuel to 15 parts per million. Furthermore, the product significantly reduces a plant's need for heated and conditioned water. The traditionally employed water-wash method necessitates either the purchase of centrifuges or the gravity-separation of the water from biodiesel.

"After transesterification, you have methyl esters that need purification," Bertram said, explaining how water washing is typically used to remove contaminants from methyl esters.

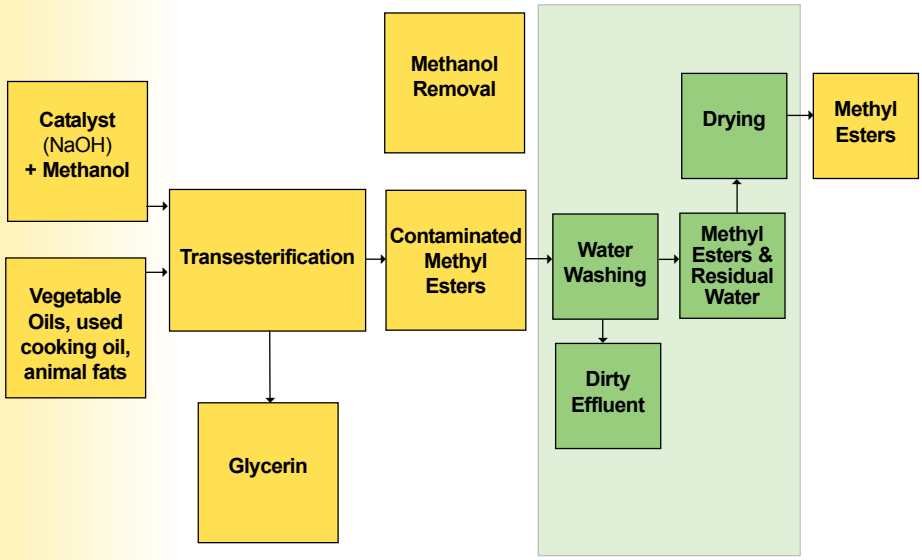
Abrams said The Dallas Group believes the water-wash method has several limitations, including decreased yields due to methyl ester loss in effluent; high soap levels that cause emulsification; high effluent treatment and disposal costs; and the time and cost of drying methyl esters. High soap levels in particular may lead to poor separation, contribute to yield losses and require multiple washes to achieve specification, Abrams said. In some cases, 24 hours are required to effect a single separation.

Additionally, it is not uncommon for producers to end up with a methyl ester/water emulsion. "Without a water-wash, there are no such emulsions formed," Abrams said. "The disposal, and even permitting of, wastewater is difficult to impossible, depending on plant location. Magnesol greatly reduces dependency on water and resultant wastewater disposal issues."

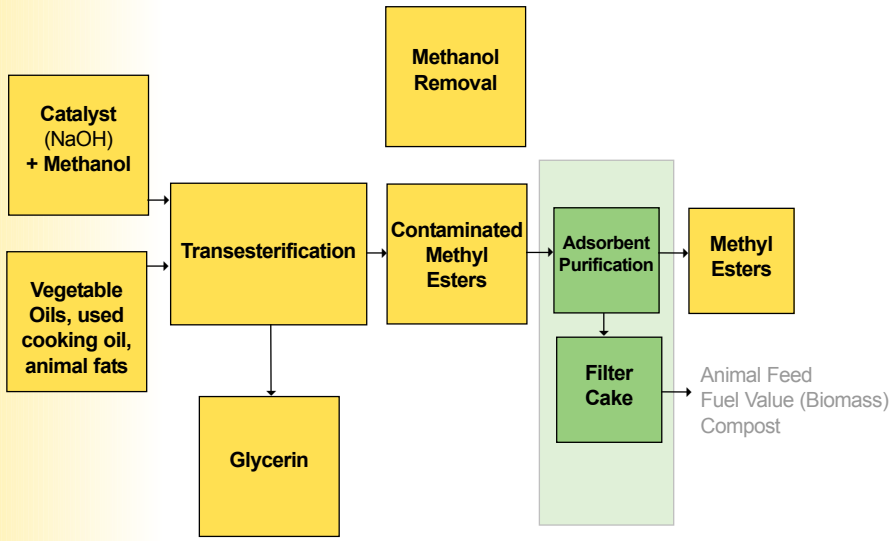
What is perhaps most attractive about Magnesol, is that it works simply and relatively inexpensively.

Cooke shared information about Magnesol at the 2005 National Biodiesel Conference & Expo in Ft. Lauderdale, Fla., in early February. His presentation—essentially a detailed explanation of how biodiesel can be purified by using the company's trademarked adsorbent—covered the basic biodiesel process, the technology of filtration (passive and active), the results of a pilot

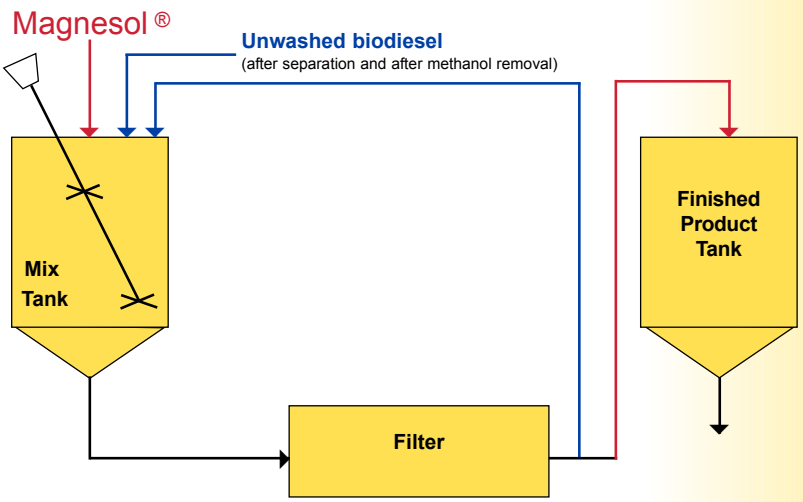
Biodiesel Production with a Water-wash Treatment




Biodiesel Production with Adsorbent Purification



## Biodiesel Purification Process




**Benefits of treatment with MAGNESOL ®**

- ✔No water-effluent stream
- ✔No emulsification
- ✔Improved oxidative stability (OSI)
- ✔Minimal yield loss
- ✔Minimal capital expenditure
- ✔Allows for continuous operation
- ✔Expedites the purification process
- ✔Adsorbs residual water

plant trial that involved the product, and a brief look at replacing the water-wash step with the company's magnesium silicate treatment.

Cooke explained that Magnesol could be used by biodiesel producers as a "total replacement" of the water wash step, or a "polishing step" used to round out the water wash treatment.

In a standard biodiesel production process, Magnesol—a fine white powder—is mixed with unwashed biodiesel in a mixing tank (for five to 10 minutes) after glycerin separation and after methanol removal.

According to Cooke, magnesium silicate has a strong affinity for polar compounds, thereby actively filtering out excess methanol, free glycerin, mono and di-glycerides and metal contaminants, in addition to free fatty acids and soap. These materials are then removed from the process through filtration. Note: Glycerin is a polar molecule, and thereby susceptible to the adsorptive abilities of magnesium silicate. That's why Magnesol is added to the process after the glycerin separation step.

Explaining the difference between "passive filtration" and "active filtration," Cooke said Magnesol has "charged sites" on its surface (areas that attract the afore mentioned unwanted polar compounds).

"Adsorptive sites may have either acidic or basic characteristics," he said, before explaining the testing methods used to measure the number—and strength—of adsorptive sites on a given amount of adsorbent matter such as Magnesol.

Cooke said testing has shown that synthetic magnesium silicate has high numbers of acidic and basic adsorptive sites, as opposed to passive filter-aid-type materials like diatomaceous earth, which "did not have any active filtration sites."

With the use of Magnesol, Cooke said, the producer is left with a potentially valuable "filter cake" rather than dirty effluent. Clients of The Dallas Group are currently exploring a variety of markets for this filter cake, and the company believes the byproduct has potential value as an animal feed supplement, a form of biomass fuel, fertilizer or compost.

### The BECON study

The Dallas Group has over 30 years experience in the purification of various chemicals, including esters and the resulting byproducts of those processes. In addition to its own in-house work on biodiesel (with outside lab confirmation), the Biomass Energy Conversion Facility (BECON) at Iowa State University performed trials comparing the traditional water-wash method to biodiesel purification with Magnesol. Results from this study were discussed by Cooke in his presentation and also by Dr. Jon Van Gerpen during a special technology session at the National Biodiesel Conference. Van Gerpen, a respected authority on the subject of biodiesel, directed the pilot study at the BECON facility. He has since taken a position at the University of Idaho as department head of Biological and Agricultural Engineering.

In that study, methyl esters were produced in 40-gallon batches from both degummed soybean oil and yellow grease

feedstocks in BECON's pilot plant reactor. In both cases, the methanol was removed from the methyl esters, but not initially water-washed.

First, 20 gallons of the soybean methyl esters were water-washed and dried, while another 20 gallons were treated at 77 degrees Celsius with 1-percent-by-weight Magnesol. After 20 minutes of mixing (longer than is probably required in a commercial plant setting, Cooke said), the purified methyl ester was filtered. The resulting biodiesel from both methods passed all specifications of ASTM D-6751. According to the study's authors, Van Gerpen and Kirk Menges, the Magnesol-treated biodiesel contained a lower soap and sodium content than the water-washed and dried sample. Furthermore, the Magnesol-treated biodiesel showed a significant improvement in oxidative stability when compared to both the original methyl esters and the water-washed and dried sample.

In a second trial, 20 gallons of the yellow grease methyl esters were water-washed and dried and 20 gallons were treated with at 77 degrees Celsius with 2-percent-by-weight Magnesol. After 20 minutes of mixing, the purified methyl ester was filtered. Like the first test with soy methyl esters, the Magnesol-treated sample of yellow grease-derived methyl esters passed all ASTM specifications while the waterwashed and dried sample did not. The Magnesol-treated biodiesel contained a lower soap and sodium content than the water-washed and dried sample. Again, the Magnesol-treated biodiesel showed a significant improvement in oxidative stability when compared to both the original methyl esters and the water-washed and dried sample.

During his presentation, Cooke concluded that the benefits of treating methyl esters with Magensol are multi-fold. He reiterated Bertram's claims about the product: With Magnesol, there is no water effluent, no emulsification, improved oxidative stability, minimal yield loss and minimal capital expenditure, all through an application that "expedites the purification process and allows for continuous operation."

Fielding questions from attendees, Cooke said the cost of using Magnesol is in the range of 1 cent to 10 cents per gallon of finished biodiesel, depending on the starting contaminant level. However, he reminded attendees that the filter cake could potentially be used as an animal feed. "It has a certain nutritional value," he said.

According to Bertram, the capital costs of transitioning a biodiesel facility to Magnesol are relatively low. That's because only a low-tech filtering system is required. In addition to potentially eliminating the drying step and the requirement for a wastewater treatment system, the use of Magnesol could replace a centrifuge, yielding additional savings of capital, time and maintenance costs.

There are less obvious savings, too, Bertram said. "Magnesol actually offers the biodiesel producer a lot of latitude in running their process," he said. "It adsorbs glycerin, free glycerin, metals, soaps, chlorophyll, residual free fatty acids, odors, color, methanol and water. Since Magnesol adsorbs such a wide range of impurities, it compensates for upstream upsets in the process, offering clean and more stable biodiesel." ■

For more information about Magnesol visit www.dallasgrp.com.

Tom Bryan is editorial director of *Biodiesel Magazine*. Reach him by e-mail at tbryan@bbibiofuels.com or by phone at (701) 746-8385.

BIODIESEL MAGAZINE

This article was printed in the 2005 March issue of *Biodiesel Magazine*.

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January 2008 www.BiodieselMagazine.com

TECHNOLOGY

# Cleaner and Clearer

In a challenging economic environment, producing a top quality product is one way to maintain a competitive edge. For biodiesel producers, that means finding the most economical way to wash and polish their crude biodiesel to the highest possible standard. Schroeder Industries says its system can produce clean biodiesel quickly and inexpensively.

By Jerry W. Kram

Pictured are before and after samples of fuel washed using Schroeder Industries Magnesol-based dry-wash system.

PHOTO: SCHROEDER INDUSTRIES

BIODIESEL
MAGAZINE

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TECHNOLOGY

Quality is the name of the game in biodiesel these days. Filter-clogging impurities made headlines in 2006 and biodiesel producers don't need adverse press in an economically demanding era. With any business, entrepreneurs rise to the challenge and create innovative and economical solutions to industry problems. "Purification is only one part of the production process and is one, in our opinion, that is too frequently overlooked," says Michael Benzies of Filtertechnik. "Industry standards are becoming increasingly stringent and upstream procedures need to be adhered to in order to be in a position to even start purifying."

A key step in producing quality biodiesel is washing to remove impurities such as excess caustic catalyst, methanol, soaps and free glycerin. Along with filter clogging, unwashed biodiesel can cause seal failures, clogged fuel injectors, damaged fuel pumps and other problems in diesel engines. In the United States, the most common method of removing these impurities is wet washing. Wet washing uses water as a solvent to carry away the impurities, leaving the pure biodiesel behind. But wet washing has disadvantages. It's a time-consuming step requiring many hours for the biodiesel and water to completely separate. Wet washing can also leave residual traces of water in the fuel. "In drier areas you may have water restrictions," Benzies says. "You may need some treatment if you have really hard water. But the real problem comes with the high levels of soaps and emulsions that form if the wet wash isn't performed properly. You then have a risk of having a very poor separation of the fuel and the water and an extended separation time. The final problem is the disposal of the hazardous effluent waste which is the byproduct of the wet wash. It may be that you have to wash seven or eight times in order to achieve clarity."

Dry washing is an alternative. In dry washing, an adsorbent is added that attracts and combines with impurities, separating them from the biodiesel. Some systems use ion exchange resins as the adsorbent (see "Waterless Washing Machine" in the May 2007 issue), while others use a mineral called magnesium silicate, one type of which is marketed under the name Magnesol by the Dallas Group of America Inc. Recently, lubricant purification specialist Schroeder Industries became the exclusive distributor for a Magnesol-based dry-wash system created by Filtertechnik. "Having looked at various dry-wash systems including competitive silicates and resin systems, we decided to run with the Magnesol product based on several factors: first and foremost, it's one of the few products that had independent verification put on it," Benzies says. "It's one of the few products that published performance data, which is absolutely vital."

## Keeping Watch

Schroeder's system works in a similar fashion to other dry-wash systems (see "Adsorbing It All" in the March 2005 issue). After crude glycerine is separated and removed, and excess methanol is vented, Magnesol powder is added to a tank of biodiesel and agitated with a mixer for about 25 minutes. The process uses 0.5 percent to 1 percent Magnesol by weight, depending on the level of contaminants in the batch of biodiesel. So, 2,000 pounds of biodiesel, which is about 265 gallons, would require 20 pounds of Magnesol. The powder attracts polar molecules and separates them from the nonpolar biodiesel. Methanol, water, glycerin and catalysts are all polar molecules. "That's effectively what happens when the Magnesol comes in contact with the crude methyl ester," Benzies says. "It adsorbs all the impurities."

After agitation, the biodiesel is circulated through Schroeder's wash columns to filter out the Magnesol and its cargo of contaminants. "Moving across to the wash stage, it is at this time when we start to see things improving in terms of visual clarity," Benzies says. "The advantage of using our systems in conjunction with Magnesol is that the towers enhance the clean-up process. At this point we see a rise in clarity for the first time. The milkiness and cloudiness that you see in your crude methyl ester is now replaced by a bright, golden crisp color."

After the biodiesel reaches the desired level of clarity, it is transferred to a final polish tank. Schoeder recommends that all biodiesel go through a polishing step to maintain stringent quality standards, irrespective of the washing method. They also encourage biodiesel producers to be rigorous with their own quality testing. "We are the only producer of filter and purification systems that actually encourage producers to do these tests simply because they don't lie to you, and will tell you exactly how good your purification method is," Benzies says.

Schroeder's polishing filter units can handle from 500 liters per hour (132 gallons per hour) to 2,500 liters per hour



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TECHNOLOGY

(661 gallons per hour) and remove residual particulates and water. An innovative part of the units is the built-in monitoring systems that include particulate counters and water monitors. The monitors display the level of contamination on liquid crystal display screens and can be downloaded to a computer for real-time monitoring and batch tracking. The system can also send e-mail alerts and even download alerts to cell phones. "Archiving traceability, building up records, having control of your production process is absolutely important," Benzies says. "If someone has problems with their vehicle they instinctively blame the fuel. That's one of the things producers have to keep in mind, they need to have some sort of in-house traceability that says that that particular batch was a good batch."

## Performance

Magnesol was compared with wet washing by researchers at Iowa State University, Benzies says. The results showed significant results after just 20 minutes of processing. "The performance data showed a massive decrease in glycerin and the moisture removal capability and methanol reduction," he says. "More importantly, if you look at the soap reduction capability, it's just staggering in a short space of time to get from a high level to an acceptable level. That is one of reasons we have embraced this dry-wash medium."

The dry-wash systems have other benefits. The cost of operating a dry-wash system is lower than a wet-wash system. Disposal and water treatment costs are also lower with a dry-wash system. Lower cost is not the biggest selling point, according to Benzies. "In our opinion, producers change from wet to dry for two reasons, speed and fuel quality" he says.

PHOTO: SCHROEDER INDUSTRIES

The BD-6000 Final Polishing Unit can be outfitted with Schroeder Particle and Moisture monitoring technology.

Filtertecknik compared biodiesel produced by its system with other commercially available fuels, with surprising results, Benzies says. "When we did particle counts on standard petrodiesel, it was shocking how dirty it turned out to be," he says. "Now we are under no illusions that it didn't leave the refinery at this cleanliness level, but with so many underground storage facilities and dirty nozzles, this is the cleanliness level that is being used in a lot of the motor vehicles today." Wet-washed biodiesel was cleaner than the petrodiesel. The dry-washed biodiesel was cleaner still, with a lower moisture level than the wet-washed biodiesel.

## Trends

Since 2004, biodiesel producers in the United Kingdom have adopted dry-wash systems. That year, 70 percent of producers used wet washing and 20 percent didn't wash their biodiesel at all. By 2006, 43 percent of producers surveyed were dry washing their biodiesel and 47 percent were still using wet-washing systems. "It wouldn't surprise me if the dry systems were to surpass the wet systems [in 2007]," Benzies says. The reasons for this shift were because wet-wash producers were experiencing problems, dry-wash systems have now come into their own and are available on the market, and industry standards have become more stringent, he says.

U.S. biodiesel producers are also interested in this new technology, says Jonathan Dugan, a product specialist with Schroeder Industries. However, with the current financial challenges facing the industry, producers are being cautious with capital investments. He says they talked to a couple of producers about developing the technology. "There has been some frustration with folks on the capital equipment side asking 'Why isn't anybody buying anything?'" Dugan says. "Until the government puts on a tax credit or we figure out a cheaper feedstock, it's a little bit of a waiting game. But if crude goes up another $20 or $30 we could see a swing where biodiesel is profitable again. At this time, people aren't interested in retrofits. They are more interested in paying for the technology they've already purchased."

In addition, many producers are hesitant to change from a well-established process. "Some of it has been slow going," Dugan says. "The acceptance has been good. But it has been confusing for some about how they would apply it. Water washing has been the de facto standard for quite some time. Adsorbent technology is new to

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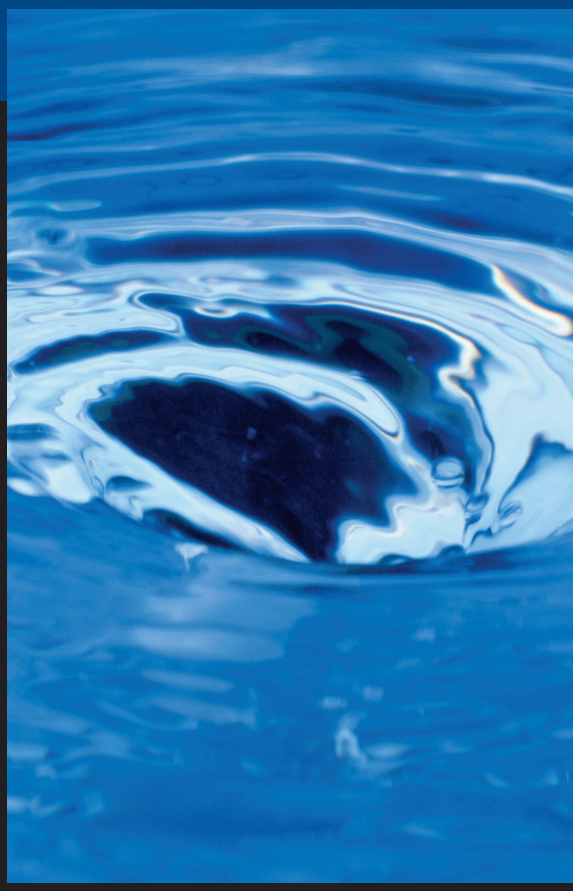

MAGNESOL® D-SOL
eliminates the need for water wash and...

- SAVES TIME…
  Purify biodiesel in minutes, not hours and with no messy emulsions.
- SAVES CAPITAL…
  No need for expensive centrifuges, dryers, or settling tanks.
- SAVES ENERGY…
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folks so we are trying to explain to them how it works and why it works and how it can save them money. But it's coming along."

Tightening water supplies, plus the cost of treating effluent in many areas of the United States will be a factor in biodiesel production, Dugan says. He described a visit to a biodiesel producer who used wet washing largely because he had a favorable agreement with the municipal water and sewer service providers. "They said if the local municipality hadn't been so gracious in helping to get the business started, they would have had to go to Magnesol and a dry-wash process," he says. "When they build their next plant, it may be a different story. It has everything to do with the local rules and government."

Despite the current challenges in the biodiesel industry, there are still a lot people interested in building new plants. These companies are taking a good hard look at using dry washing, Dugan says. "We have spoken to a lot of folks," he says. "We have our systems specified into a lot of medium-sized plants and we're talking to some of the larger plants. I think that as soon as it makes sense to build up the industry capacity, we will see an influx of business that we can't even imagine. That's really exciting for us." ■

Jerry W. Kram is a *Biodiesel Magazine* staff writer. Reach him at jkram@bbibiofuels.com or (701) 738-4962.

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# ANNEX VI: CENTRIFUGE AND AC DRIVE

## 1.Centrifuge

The centrifuge used in the different trials is a Basic Raw Power Centrifuge, which is manufactured by WVO Designs. Its main characteristics, which can be found in http:// wvodesigns.com/ are the following:

- The Basic Raw Power Centrifuge runs at 3450rpm and produces over 1200Gs.
- This entry level centrifuge is the lowest cost way to get out of filtering waste oil. Consider the optional bolt-on heater to increase flow rates to 15gph.
- Single Pass: Adjust flow rate to suit your feedstock and cleaning requirements
- Quiet: Custom US Made Motor operates smooth and quiet(it will be quieter than an A/ C Unit)
- No Pressure: High pressure pumps and fittings are expensive and leaks costly
- Direct Drive: Rotor speed is unquestionable and you can't get a simpler design
- High Capacity: Rotor holds over half a litre so you can remove pounds of GUNK and clean hundreds of gallons between cleanings
- Modular Design: Start with the basic unit and upgrade as your needs require

Different videos about how is it assembled and how does it work can be found in the next links:

http://vimeo.com/8238179

http://www.youtube.com/watch?v=cUhgKFV5Ri4

http://www.youtube.com/watch?v=5cvQazPlzKU

http://www.youtube.com/watch?v=pagHQKvaC9k

# 2.AC Drive

A GS1 AC Drive was used as a motor drive for the centrifuge. In this way, the rpm of the centrifuge could be maximised up to 6000 rpm and the spinning speed could also be controlled with it. In the next pages the complete overview of the drive is attached.

# GS1 Series Introduction

| GS1 Series Drives | | | | | |
|---|---|---|---|---|---|
| Motor Rating | Hp | .25 | .5 | 1 | 2 |
| | kW | 0.2 | 0.4 | 0.75 | 1.5 |
| 115 Volt Single-Phase Input/230 Volt Three-Phase Output | | ✔ | ✔ | | |
| 230 Volt Single-Phase Input/230 Volt Three-Phase Output | | ✔ | ✔ | ✔ | |
| 230 Volt Three-Phase Input/Output | | | | | ✔ |

## Overview

The GS1 series of AC drives is our most affordable and compact inverter, offering V/Hz control with general purpose application features. These drives can be configured using the built-in digital keypad (which also allows you to set the drive speed, start and stop, and monitor specific parameters) or with the standard RS-485 serial communications port. Standard GS1 features include one analog input, four programmable digital inputs and one programmable normally open relay output.

## Features

- Simple Volts/Hertz control
- Pulse Width Modulation (PWM)
- 3 – 10 kHz carrier frequency
- IGBT technology
- 130% starting torque at 5Hz
- 150% rated current for one minute
- Electronic overload protection
- Stall prevention
- Adjustable accel and decel ramps
- S-curve settings for acceleration and deceleration
- Manual torque boost
- Automatic slip compensation
- DC braking
- Built-in EMI filter
- Three skip frequencies
- Trip history
- Integral keypad and speed potentiometer
- Programmable jog speed
- Three programmable preset speeds
- Four programmable digital inputs
- One programmable analog input
- One programmable relay output
- RS-485 Modbus communications up to 19.2K
- Optional Ethernet communications
- UL/cUL/CE listed

## Accessories

- AC line reactors
- RF filter
- Ethernet interface
- Four and eight port RS-485 multi-drop termination board
- KEP***Direct*** I/O Server
- GSoft drive configuration software
- GS-485HD15-CBL - ***ZIP***Link RS485 Communication cable for connection to the DL06 and D2-260 15-pin ports.

***Detailed descriptions and specifications for the accessories are available in the "GS/DURAPULSE Accessories" section.***

## Typical Applications

- Conveyors
- Fans
- Pumps
- Shop tools

## GS1 series part numbering system

GS1 - 2 0P5

**Applicable Motor Capacity**

0P2: 1/4hp
0P5: 1/2hp
1P0: 1hp
2P0: 2hp

**Input Voltage**

1: 100-120VAC
2: 200-240VAC

**Series Name**

# GS1 Series Specifications

| 115V/230V CLASS GS1 Series | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***Model*** | | ***GS1-10P2*** | ***GS1-10P5*** | ***GS1-20P2*** | ***GS1-20P5*** | ***GS1-21P0*** | ***GS1-22P0*** |
| ***Price*** | | <---> | <---> | <---> | <---> | <---> | <---> |
| ***Motor Rating*** | ***HP*** | 1/4 hp | 1/2 hp | 1/4 hp | 1/2 hp | 1hp | 2hp |
| | ***kW*** | 0.2 kW | 0.4 kW | 0.2 kW | 0.4 kW | 0.7 kW | 1.5 kW |
| ***Rated Output Capacity (200V) kVA*** | | 0.6 | 1.0 | 0.6 | 1.0 | 1.6 | 2.7 |
| ***Rated Input Voltage*** | | Single-phase 100-120 VAC ±10%, 50/60 Hz ±5% | | Single/three-phase: 200-240 VAC±10%, 50/60 Hz ±5% | | | Three-phase: 200-240 VAC±10%, 50/60 Hz ±5% |
| ***Rated Output Voltage*** | | Three-phase corresponds to double the input voltage | | Three-phase corresponds to the input voltage | | | |
| ***Rated Input Current (A)*** | | 6 | 9 | 4.9/1.9 | 6.5/2.7 | 9.7/5.1 | 9 |
| ***Rated Output Current (A)*** | | 1.6 | 2.5 | 1.6 | 2.5 | 4.2 | 7.0 |
| ***Watt Loss @ 100% I (W)*** | | 19.2 | 19.2 | 18.4 | 26.8 | 44.6 | 73 |
| ***Weight: kg (lb)*** | | 2.10 | 2.20 | 2.20 | 2.20 | 2.20 | 2.20 |
| ***Dimensions (HxWxD) (mm [in])*** | | 132.0 x 68.0 x128.1 [5.20 x 2.68 x 5.04] | | | | | |
| **Accessories** | | | | | | | |
| ***Ethernet Communications module for GS Series Drives (DIN rail mounted)*** | | GS-EDRV | | | | | |
| ***Four port RS-485 multi-drop termination board*** | | GS-RS485-4 | | | | | |
| ***Eight port RS-485 multi-drop termination board*** | | GS-RS485-8 | | | | | |
| ***Software*** | | GSoft / KEP*Direct* | | | | | |
| ***OPC Server*** | | KEP*Direct* | | | | | |

# GS1 General Specifications

| General Specifications | | | |
|---|---|---|---|
| ***Control Characteristics*** | | | |
| ***Control System*** | | | Sinusoidal Pulse Width Modulation, carrier frequency 3kHz - 10kHz |
| ***Rated Output Frequency*** | | | 1.0 to 400.0 Hz limited to 9999 motor rpm |
| ***Output Frequency Resolution*** | | | 0.1 Hz |
| ***Overload Capacity*** | | | 150% of rated current for 1 minute |
| ***Torque Characteristics*** | | | Includes manual torque boost, auto-slip compensation, starting torque 130% @ 5.0Hz |
| ***DC Braking*** | | | Operation frequency 60-0Hz, 0-30% rated voltage. Start time 0.0-5.0 seconds. Stop time 0.0-25.0 seconds |
| ***Acceleration/Deceleration Time*** | | | 0.1 to 600 seconds (can be set individually) |
| ***Voltage/Frequency Pattern*** | | | V/F pattern adjustable. Settings available for Constant Torque - low and high starting torque, Variable Torque - low and high starting torque, and user configured |
| ***Stall Prevention Level*** | | | 20 to 200% or rated current |
| ***Operation Specification*** | | | |
| ***Inputs*** | ***Frequency Setting*** | ***Keypad*** | Setting by <UP> or <DOWN> buttons or potentiometer |
| | | ***External Signal*** | Potentiometer - 5kΩ 0.5W, 0 to 10 VDC (input impedance 47kΩ), 0 to 20 mA / 4 to 20 mA (input impedance 250Ω), Multi-function inputs 1 to 3 (3 steps, JOG, UP/DOWN command), RS485 communication setting |
| | ***Operation Setting*** | ***Keypad*** | Setting by <RUN>, <STOP> buttons |
| | | ***External Signal*** | DI1, DI2, DI3, DI4 can be combined to offer various modes of operation, RS485 communication port |
| ***Outputs*** | ***Multi-Function Input Signal*** | | Multi-step selection 0 to 3, Jog, Accel/decel inhibit, First/second accel/decel switch, Counter, PLC operation, External base block (N.C., N.O.) selection |
| | ***Multi-Function Output Signal*** | | AC drive operating, Frequency attained, Non zero speed, Base Block, Fault indication, Local/remote indication, PLC operation indication |
| | ***Operating Functions*** | | Automatic voltage regulation, S-curve, Over-voltage stall prevention, DC braking, Fault records, Adjustable carried frequency, Starting frequency setting of DC braking, Over-current stall prevention, Momentary power loss restart, Reverse inhibition, Frequency limits, Parameter lock/reset |
| ***Protective Functions*** | | | Overcurrent, overvoltage, undervoltage, electronic thermal motor overload, Overheating, Overload, Self testing |
| ***Operator Interface*** | ***Operator Devices*** | | 5-key, 4-digit, 7-segment LED, 3 status LEDs, potentiometer |
| | ***Programming*** | | Parameter values for setup and review, fault codes |
| | ***Parameter Monitor*** | | Master Frequency, Output Frequency, Scaled Output Frequency, Output Voltage, DC Bus Voltage, Output Direction, Trip Event Monitor, Trip History Monitor |
| | ***Key Functions*** | | RUN/STOP, DISPLAY/RESET, PROGRAM/ENTER, <UP>, <DOWN> |
| ***Environment*** | ***Enclosure Rating*** | | Protected chassis, IP20 |
| | ***Ambient Operating Temperature*** | | -10° to 40°C (14°F to 104°F) w/o derating |
| | ***Storage Temperature*** | | -20° to 60 °C (-4°F to 140°F) during short-term transportation period) |
| | ***Ambient Humidity*** | | 0 to 90% RH (non-condensing) |
| | ***Vibration*** | | 9.8 m/s$^2$(1G), less than 10Hz. 5.88 m/s$^2$ (0.6G) 20 to 50 Hz |
| | ***Installation Location*** | | Altitude 1000m or lower above sea level, keep from corrosive gas, liquid and dust |
| ***Options*** | | | Programming Software (GSOFT) |

# GS1 Specifications - Installation

Understanding the installation requirements for your GS1 drive will help to ensure that it will operate within its environmental and electrical limits.

***NOTE:***
***Never use only this catalog for installation instructions or operation of equipment; refer to the user manual, GS1-M.***

| Environmental Specifications | |
|---|---|
| ***Protective Structure*** | IP20 |
| ***Ambient Operating Temperature[2]*** | -10 to 40°C |
| ***Storage Temperature[3]*** | -20 to 60°C |
| ***Humidity*** | to 90% (no condensation) |
| ***Vibration[4]*** | 5.9 m/s$^2$ (0.6g), 10 to 55 Hz |
| ***Location*** | Altitude 1,000 m or less, indoors (no corrosive gases or dust) |

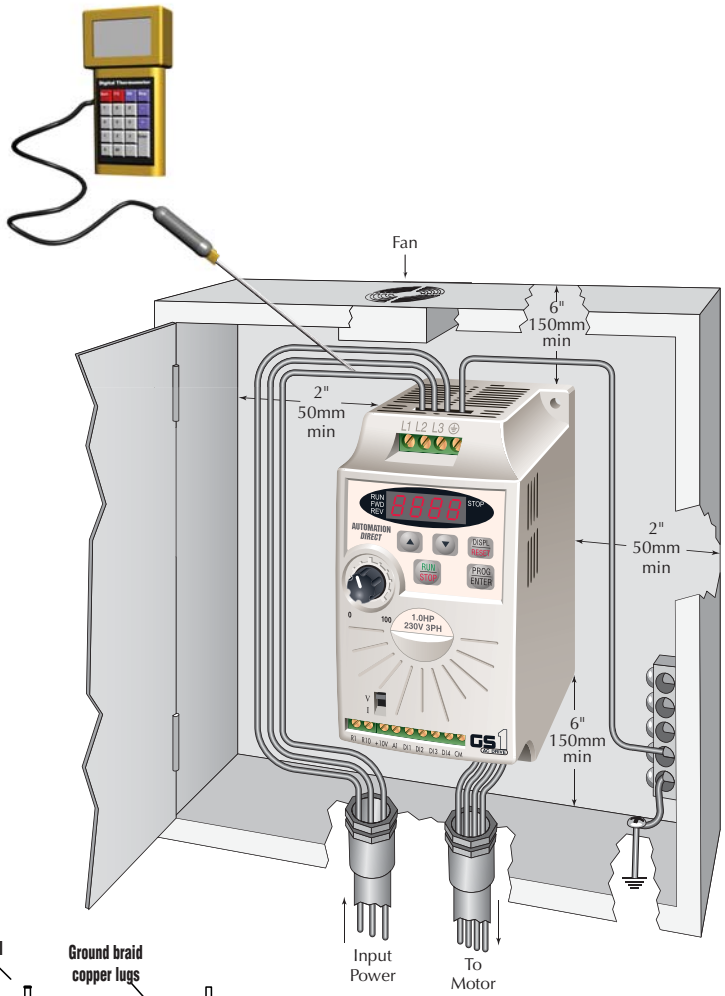
***1: Protective structure is based upon EN60529***

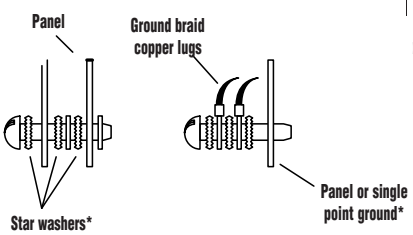
***2: The ambient temperature must be in the range of -10° to 40° C. If the range will be up to 50° C, you will need to set the carrier frequency to 2.1 kHz or less and derate the output current to 80% or less. See our Web site for derating curves.***

***3: The storage temperature refers to the short-term temperature during transport.***

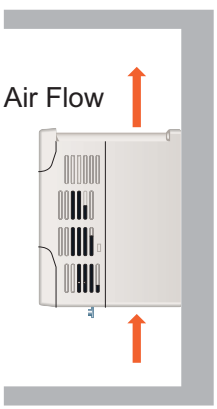
***4: Conforms to the test method specified in JIS CO911 (1984)***

| Watt-loss Chart | |
|---|---|
| ***GS1 Drive Model*** | ***At full load*** |
| ***GS1-10P2*** | 19.2 |
| ***GS1-10P5*** | 19.2 |
| ***GS1-20P2*** | 18.4 |
| ***GS1-20P5*** | 26.8 |
| ***GS1-21P0*** | 44.6 |
| ***GS1-22P0*** | 73 |



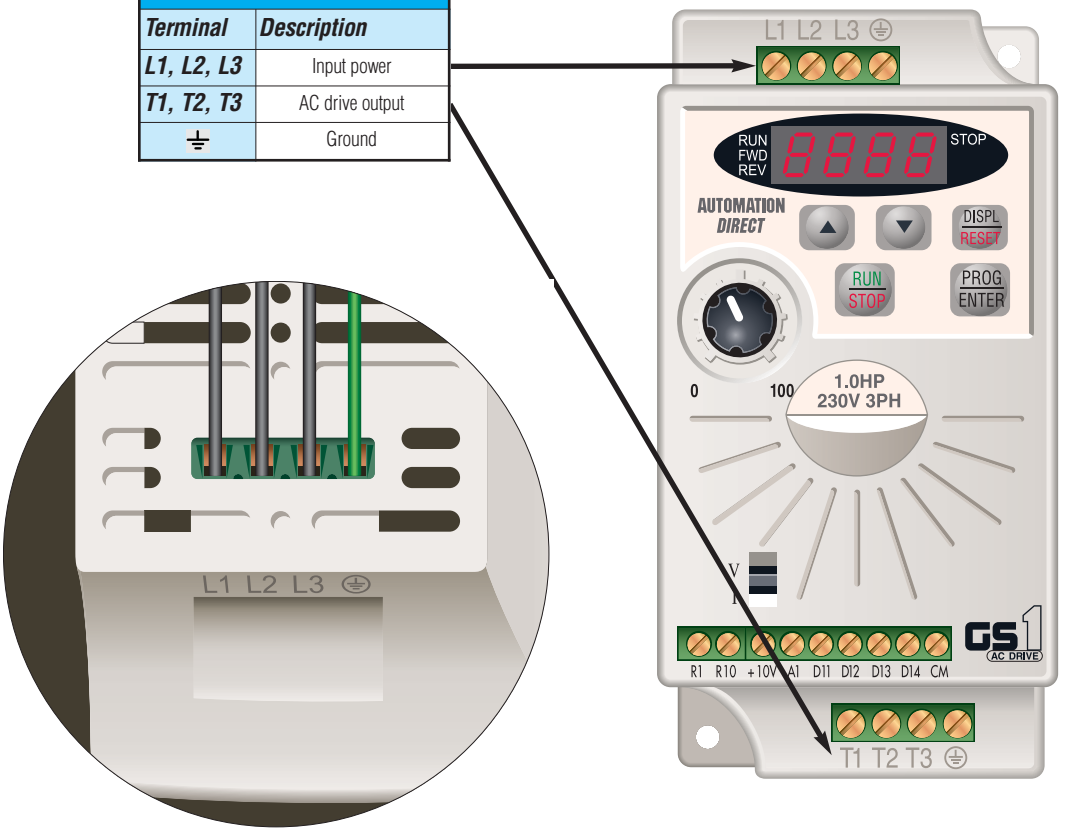

** FOR PAINTED SUB-PANELS, SCRAPE THE PAINT FROM UNDERNEATH THE STAR WASHERS BEFORE TIGHTENING THEM.*




**Warning: AC drives generate a large amount of heat, which may damage the AC drive. Auxiliary cooling methods are typically required in order to not exceed maximum ambient temperatures.**

# GS1 Specifications - Terminals

| Main Circuit Wiring | |
|---|---|
| ***Terminal*** | ***Description*** |
| ***L1, L2, L3*** | Input power |
| ***T1, T2, T3*** | AC drive output |
| ⏚ | Ground |




| Control Circuit Terminals | |
|---|---|
| ***Terminal Symbol*** | ***Description*** |
| ***R10*** | Relay output 1 normally open |
| ***R1*** | Relay output 1 common |
| ***DI1*** | Digital input 1 |
| ***DI2*** | Digital input 2 |
| ***DI3*** | Digital input 3 |
| ***DI4*** | Digital input 4 |
| ***AI*** [1] | Analog input |
| ***+10V*** | Internal power supply (10 mA @ 10 VDC) |
| ***CM*** | Common |

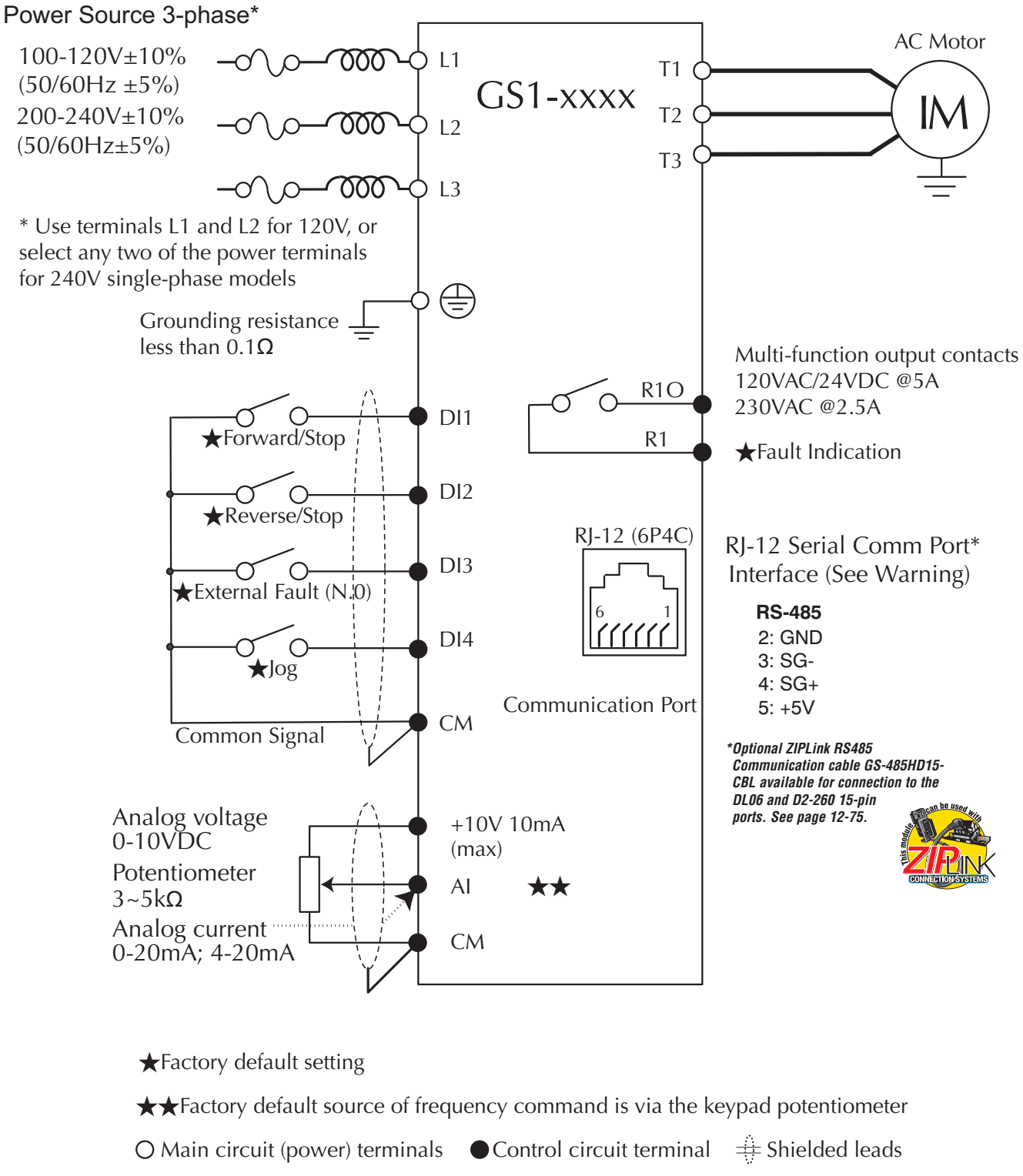
*[1] 0 to +10 VDC, 0 to 20 mA, or 4 to 20 mA input represents zero to maximum output frequency.*

***Note:*** *Use twisted-shielded, twisted-pair or shielded-lead wires for the control signal wiring. It is recommended all signal wiring be run in a separate steel conduit. The shield wire should only be connected at the drive. Do not connect shield wire on both ends.*

# GS1 Specifications - Basic Wiring Diagram

***Note: Users MUST connect wiring according to the circuit diagram shown below. (Refer to user manual GS1-M for additional specific wiring information.)***

***Note: Refer to the following pages for explanations and information regarding line reactors and RF filters: 13-50, 13-67.***



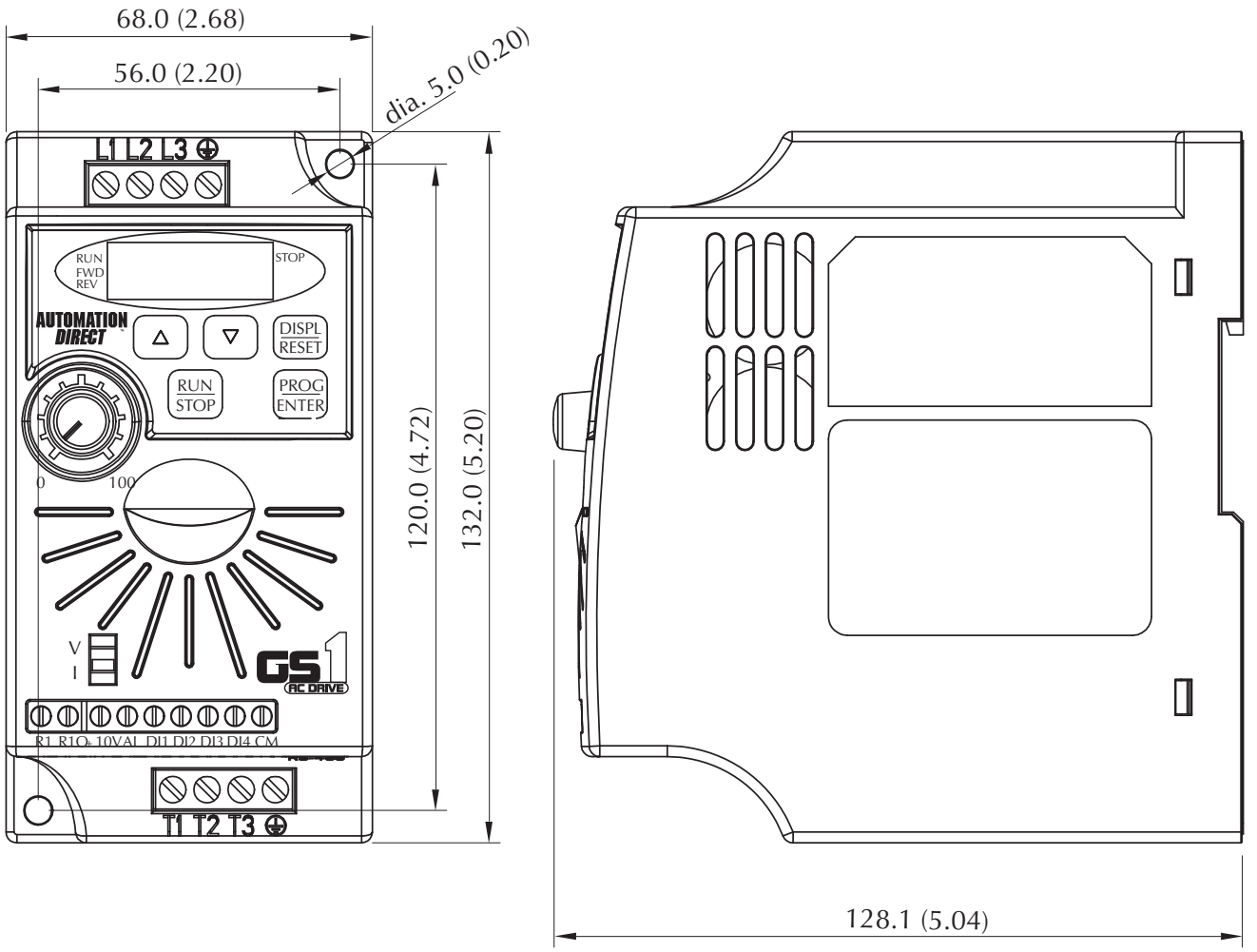

★Factory default setting

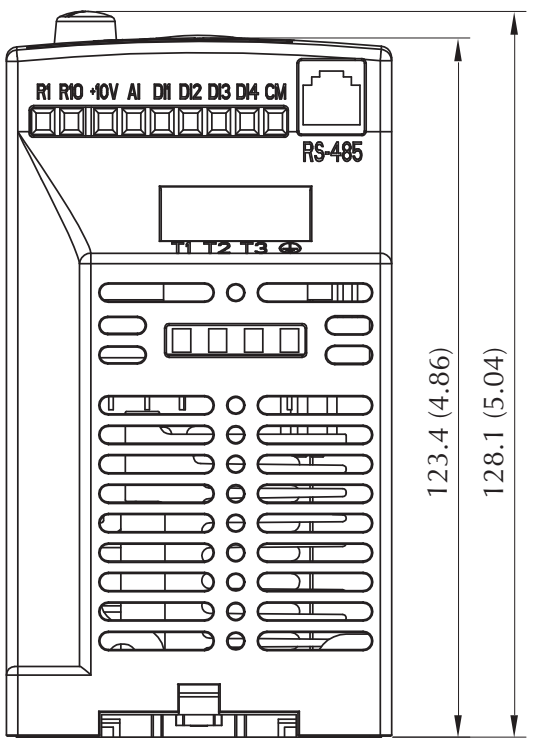
★★Factory default source of frequency command is via the keypad potentiometer

○ Main circuit (power) terminals ● Control circuit terminal ⫩ Shielded leads

**WARNING: Do not plug a modem or telephone into the GS1 RJ-12 Serial Comm Port, or permanent damage may result. Terminals 2 and 5 should not be used as a power source for your communication connection.**

# GS1 Specifications - Dimensions




Unit: mm (in)